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# GEOCHIMICA ET COSMOCHIMICA ACTA



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# Geochemical changes due to weathering under varying climatic conditions

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(*Received* 26 *January* 1955)

ABSTRACT

Nine soil profiles from New Zealand, developed on arkosic parent material and under varying climatic conditions, were investigated, using mechanical, microscopical, X-ray, differential thermal, chemical, and spectrographic methods of analysis. It is found that, with an increase in annual temperature, the percentage of clay rises and of organic matter falls. The processes responsible for formation of clay minerals are shown to be more active at depth than in the surface horizons, and hence percentage clay curves and percentage clay mineral curves may depart widely from each other in their angles of slope. With increase in temperature, larger quantities of kaolinite are formed, while under cooler conditions hydrous mica becomes more prominent. The chemical analyses reveal that effects of weathering are more readily observable in silt fractions than in clay fractions. The distribution of major and minor elements are related to the geochemical laws in terms of precipitation, adsorption, camouflage, and capture, and the influence of organic matter is also discussed. Relationships between concentration of minor elements and climatic conditions are considered, and it would seem that generally an increase in temperature means loss of minor elements with the exception of zirconium and yttrium.

## Introduction

It is generally accepted that, in the formation of soils, there are five independent variables (Jenny, 1941) which affect the constitution and composition of any one soil system. These are climate, organisms, topography, parent material, and time. In the study of the effectiveness of any one of these, the other four must be kept constant.

Samples of soil profiles were collected from four fairly widely separated regions in New Zealand. In all cases the parent material was arkosic in nature, and mineralogically all samples were almost exactly alike. The vegetation on the soils was either a typical beech forest or grass, and in this latter case forest clearing had taken place very recently. The surrounding topography varied from rolling to steep, i.e., from an angle of 10° to 30°. In most cases, the profiles collected were taken from locally flatter regions, and usually the angle of slope did not exceed 10°. Judging from the pronounced stratification present in the soil bodies, soil creep has not occurred. Profiles of mature podzols and immature soils were collected from similar climatic regions, and, from the differences between these, some idea of the influence of strong leaching can be computed.

The following climatic data have been obtained by extrapolation of data from meteorological stations. In only one case, viz., Canterbury mature, was great extrapolation needed, for there were no meteorological data obtainable for this particular region.

| | Mean temp. (°F) | Annual rainfall in inches |
|---|---|---|
| Profile 1—North Auckland immature | 57·0 | 55 |
| Profile 2—North Auckland mid semi-mature | 57·5 | 58 |
| Profile 3—North Auckland mature | 57·0 | 57 |
| Profile 4—Wellington immature | 51·1 | 60 |
| Profile 5—Wellington mature | 49·0 | 60 |
| Profile 6—Canterbury immature | 50·0 | 47 |
| Profile 7—Canterbury mature | 43·3 | 70 |
| Profile 8—Southland immature | 49·6 | 35 |
| Profile 9—Southland mature | 49·6 | 37 |

The differences of temperature, while small when mean temperatures are considered, become much greater when monthly averages are considered, and this must be borne in mind when climatic data are assessed.

## Description of the Samples Collected

The following is a description of the appearance of the various soil horizons in the field, together with other data pertinent to the locality. Names given to the samples are those from the surrounding area. Textures cited are from field experimental techniques. Series names are those used by the New Zealand Soil Bureau.

*Profile* 1—*North Auckland immature*

Locality: Whangerei County, Opuawhanga Survey District, 1½ miles north of Tutukaka, on the Tutukaka Matapouri Bay Road. Height above sea-level: 250 ft. Slope: 16° to 18°. Vegetation: formerly forest of the broadleaf podocarp series; now in paspalum and some bracken fern (*Pteridium* sp.). Series: Marua clay loam; 0 to 2 in.—darkish brown crumbly clay loam 8 to 12 in.—yellow-brown moderately compact clay loam to clay; 20 to 26 in.—bright yellow-brown crumbly clay loam, moderately compact; 66 to 72 in.—pinkish-red clay loam matrix surrounding well-decomposed arkosic fragments; 156 to 162 in.—pinkish-red decomposed arkosic material; 192 in.—samples of arkosic parent material.

*Profile* 2—*North Auckland mid semi-mature*

Locality: Whangarei County, Opuawhanga Survey District, 1½ miles along Jubilee Road from Marua Road, 2 miles N.E. of Marua school. [Sheet N.20, 189 × 19.] Height above sea-level: 500 ft. Slope: 10°. Vegetation: stunted *Leptospernum scoparium* with remnants of Kauri stumps, the Kauri being fairly recently removed. Series: Rangiora silty clay loam; 0 to 4 in.—dark brownish-grey silty clay loam; 4 to 7 in.—light yellow-brown clay with fairly strong iron and grey mottling, moderately compact; 11 to 22 in.—yellow-brown clay with strong iron and grey mottling, more compact; 29 to 32 in.—yellow-brown clay with faint iron and grey mottling, very compact; 38 to 44 in.—whitish-grey clay loam with pinkish mottling; 58 to 61 in.—pinkish-red clay loam; 72 in.—pinkish clay loam; 180 to 192 in.—yellow-brown clay loam with iron mottling; 300 in.—arkosic parent material.

*Profile* 3—*North Auckland mature*

Locality: Whangarei County, Hukerenui Survey District. 2 miles N.W. of Ruapekapeka trig., 4·6 miles S.E. of Kawa Kawa, on the Ruapekapeka Kawa Kawa Road. Grid 163 × 32. Height above sea-level: 720 ft. Slope: 5° to 6°. Vegetation: *Leptospernum scoparium*, a little *Dracophillium* and *Lycopodium* moss. Former cover, Kauri. Series: Hukerenui silt loam; 0 to 6 in.—dark grey structureless silt loam; 7 to 9 in.—light ash-grey structureless silt loam; 9 to 11½ in.—darkish ash-grey partly cemented and humus-stained silt loam; 12 to 14½ in.—iron pan horizon; 24 to 28 in.—bright yellow-brown clay to clay loam, moderately compact (root fissures frequent); 42 to 48 in.—pink clay. In this sample, weathering was so pronounced that no undecomposed parent material could be obtained.

*Profile* 4—*Wellington immature*

Locality: Wellington Province, Akatarawa Survey District. Section 397, block 6. Side road from the Akatarawa-Waikanae Road. Height above sea-level: 800 ft. Slope: 25°. Vegetation: forest very recently cleared; now in pasture (bracken fern). Series: Wakatikei silt loam; 0 to 9 in.—dull yellow-brown silt loam; 10 to 16 in.—light yellow-brown heavy silt loam; 18 to 24 in.—yellow-brown stony loam; 24 to 30 in.—shattered arkosic material; 50 in.—arkosic rock.

*Profile 5—Wellington mature*

Locality: Wellington Province, Akatarawa Survey District. Section 398, block 6. Summit of road to left after turn off to Akatarawa-Waikanae Road. Height above sea-level: 1400 ft. Slope: 16° to 18°. Vegetation: forest very recently cleared, *Weinmannia racemosa* and *Dacyrdium cupressinum*; now in pasture. Series: Akatarawa silt loam; 0 to 6 in.—dark black silt loam, with decomposing roots; 6 to 8 in.—black to buff grey heavy silt loam; 8 to 12 in.—black to brown silt loam; 12 ± 1/4 in.—iron pan; 12 to 16 in.—Brownish-yellow loam; 24 to 26 in.—powdery yellow silt loam; 40 to 44 in.—powdery yellow silt loam; 54 in.—weathered arkosic rock.

*Profile 6—Canterbury immature*

Locality: Canterbury Province, Hanmer, 50 yd up Jolly's pass road from the forestry observation point junction. Height above sea-level: 1940 ft. Slope: 27°. Vegetation: *Leptospernum scoparium*, mountain flax, and much silver tussock, moss and Yorkshire fog. Series: Hurunui silt loam: 0 to 1½ in.—brown loam with much admixture of grass roots; 2 to 11 in.—brown silt loam; 11 to 15 in.—yellow-brown loam; 16 to 21 in.—dull yellowish silt loam; 28 to 32 in.—yellow-brown sandy silt loam; 36 in.—arkosic parent material showing no decomposition.

*Profile 7—Canterbury mature*

Locality: Canterbury Province, 75 yd on the Canterbury side of the summit of the Lewis pass road. Height above sea-level: 2,820 ft. Slope: 30°. Vegetation: beech forest. Series: Haast sandy loam; 0 to 1 in.—forest litter; 1 to 4 in.—dark black, peaty, humus horizon; 5 to 7 in.—ashen to buff grey sandy loam; 10 to 15 in.—dull yellow grey sandy loam; 30 in.—ashen-grey gravelly material; 36 in.—arkosic rock.

*Profile 8—Southland immature*

Locality: Southland, Balclutha-Owaka area. Sheet 179, 1 mile/inch 479 × 041. Height above sea-level: 70 ft. Slope: 5° to 10°. Vegetation: forest cleared 20 yr previously and now in grass; cocksfoot, Yorkshire fog, vernal and browntop association. 0 to 4 in.—chocolate-brown free silt loam; 5 to 8 in.—yellow-brown silt loam; 11 to 16 in.—dull yellow-brown loam; 28 to 33 in.—light yellow loam; 48 in.—arkosic rock.

*Profile 9—Southland mature*

Locality: Soutland-Owaka area. Gibbs Hill. Sheet 184, 1 mile/inch 368 × 956. Height above sea-level: 100 ft. Slope: 15°. Vegetation: broadleaf-podocarp forest. (*Weinmannia racemosa*, *Dacrydium cupressinum*, etc.); 0 to 6 in.—chocolate-brown to black humus rich horizon; 6 to 12 in.—chocolate-brown to black humus rich horizon; 12 to 18 in.—chocolate-brown silt loam; 20 in.—iron pan; 20 to 26 in.—light-yellow free loam; 28 in.—arkosic parent material.

## Nature of the Parent Material

The samples of arkosic parent material and specimens of rocks occurring in soil horizons were sectioned and investigated by microscopical means. In all the cases examined the material was remarkably uniform in composition, and a general description suffices for all the samples.

In hand specimens the rocks range from ashen grey to dark grey in colour, and in some cases fragments of comminuted plant detritus can be observed. Sometimes these rocks are seamed with small quartz veinlets, but these never attain large dimensions.

In thin sections the minerals are markedly angular: only occasionally are any rounded grains to be seen, and it is considered that these grains have been rendered smooth in a previous sedimentary cycle. The minerals composing the

rock consist almost entirely of quartz and feldspar. The relative percentages vary slightly, but usually the ratio is 35 per cent quartz to 55 per cent feldspar or its decomposition products. In some cases the quartz shows the lined effect so typical of mylonitized rocks, but always the extinction is undulose in at least some grains. Shreds of biotite are also present, always bleached and often chloritized. In many specimens fragments of volcanic rock occur, showing either marked flow structure of trachytic affinities, or recrystallizing spherulites. Where determinable, the feldspar laths in these structures are albitic in nature. The accessories in the rocks are zircon, sphene, iron-ore, and occasional well-rounded garnets. The iron-ore is titaniferous in nature, for it is often associated with veins of leucoxene or dusty sphene. The zircons are small but quite euhedral, and appear to have suffered little abrasion during the deposition of the sediment. The groundmass is very fine grained and sometimes iron-stained. It appears to be micaceous in nature, and is believed to be the sericitic product of feldspar decomposition. The feldspar present in the rocks is untwinned and always cloudy due to decomposition. Wherever optic signs have been taken and refractive index measurements made, the feldspar is plagioclase, albitic in nature, and never containing more than 8 per cent of the anorthite molecule. Some orthoclase does occur, as well as occasional crystals of microcline, but the sodic-bearing plagioclase is much greater in amount than the potassium feldspars.

After deposition, these rocks suffered compaction and deformation. It was during this orogenesis that the feldspar was shattered and partially decomposed, the quartz had impressed upon it the undulose extinction, and the biotite was wrapped about the gains of feldspar and quartz, and drawn out into flaser-like structures. The decomposition of the feldspar concomitant on this cataclasis can be seen most readily in the cloudiness of these minerals. It seems that the plagioclase may originally have carried a larger quantity of the anorthite molecule, for clinozoisite is always present, either in the mineral grains following the curved cleavages, or as irregular reticulated networks representing a badly decomposed grain. In only a few cases is there any marked entry of the iron molecule into the composition of this clinozoisite, and where this does occur the association with chlorite suggests that here the mineral has been formed, at least in part, from the disintegration of some ferromagnesian mineral (probably biotite). Along with the clinozoisitic decomposition product there is a felted meshwork which is believed to be sericite, but it is usually so small in grain size that positive identification is difficult. In one sample from the Wellington area veinlets of clinozoisite were observed (profile 5, 72 in.), and these seem to be caused by percolating water. It appears that calcium is easily removed from the rock and redeposited as clinozoisite. In those rock samples occurring in the soil horizons, it can be observed that the number of hydrated iron oxide veinlets increases as the surface is approached.

Some sand and silt fractions separated from the soil profiles were examined by microscopical means. In all cases the feldspar was badly decomposed and usually iron-stained. The other predominant mineral was quartz. In the highly altered northern samples quartz was the only mineral determined with any certainty, for the feldspars had completely decomposed. In the samples examined,

there was, as would be expected, inclusion of foreign material brought by aerial transport, Numerous other workers have noted this factor, and from all corners of the world (ALEXANDER, 1934; TATARINOV, 1946; GRANGE, 1931). The main source of contaminants in the samples from the northern island is ash showers from the volcanic region. Occasional hypersthene has come from the central volcanoes (Ruapehu-Tongariro group) and rare basaltic hornblende from the western volcanic centre (Egmont). The samples collected from the southern island are contaminated to some extent by wind-borne glacial detritus. As the mountain ranges are composed essentially of arkosic material, this contamination is not believed to cause any real difference in altering the nature of the soil parent material. Actually, it was with this in mind that arkose was chosen as a parent material The accession of new material, which is always slowly taking place, would alter the factor "Time" in the variables controlling soil formation. As the soil profiles were never very deep, and also because well stratified podzols could be formed under the requisite conditions, it is considered that the addition taking place is small, and does not materially alter the soil forming processes as compared with the other factors involved. A sample of a loess-like deposit which underlay a soil profile was collected, and it was partially analyzed and compared with a partial rock analysis from one of the Southland profiles (No. 8).

| | *Loess-like material* | *Southland Rock at 48 inches (profile 8)* |
|---|---|---|
| | *per cent* | *per cent* |
| $SiO_2$ | 64·44 | 65·20 |
| $R_2O_3$ | 22·83 | 21·26 |
| CaO | 1·00 | 1·85 |
| MgO | 0·63 | 0·24 |

The only really significant difference is a higher content of lime in the rock than in the loess-like material. The greater lime content is placed as due to clinozoisite from the small amount of anorthite originally present in the feldspar. The increase in magnesia in the loess is probably a reflection of an increase in micaceous matter.

The dusting of ash from the volcanoes may possibly have affected the composition of the Akatarawa profiles (Nos. 4 and 5), for the material added would be of a more basic composition. It is believed that podzol formation would outstrip and swallow up most of the material. Furthermore, the profiles in this region can be quite shallow, and so it is believed that no great addition has taken place [as will be shown later, the feldspar added would be converted to either a micaceous mineral or kaolinite, and the ferromagnesians would probably go via chlorite to a hydrous mica]. From the evidence obtained, very drastic addition of some very foreign material would have to occur to the three most northern profiles to cause any reconstitution of the profile, for these soils would swallow up any addition, converting it to kaolinite and quartz, or allowing it to escape in solution.

The chemical analysis of the parent rocks from the various profiles are presented in Table 1. It will be seen that there is a general similarity between the various

specimens. The values which show perhaps the greatest variations are those for Ca. As calcium is amongst the first elements to be removed during leaching, the differences do not affect the course of weathering seriously. The differences

*Table* 1. *Major and minor elements present in arkoses*

| † | 1 | 2 | 4 | 5 | 6 | 7 | 8 | 9 | *S* | Å |
|---|---|---|---|---|---|---|---|---|---|---|
| $Si^{+4}$ . $10^2$ | 2699 | 2858 | 3299 | 2881 | 3142 | 3380 | 3038 | 2830 | — | 0·42 |
| $Al^{+3}$ . $10^2$ | 1025 | 963 | 797 | 1056 | 781 | 749 | 851 | 870 | — | 0·51 |
| $Ti^{+4}$ . $10^2$ | 46 | 52 | 29 | 46 | 40 | 28 | 40 | 47 | — | 0·68 |
| $Fe^{+3}$ . $10^2$ | 495 | 343 | 243 | 355 | 318 | 222 | 357 | 448 | — | 0·64 |
| $Mg^{+2}$ . $10^2$ | 38 | 28 | 39 | 46 | 46 | 16 | 8 | 50 | — | 0·66 |
| $Mn^{+2}$ . $10^2$ | 7 | 5 | 4 | 2 | 2 | 2 | 2 | 4 | — | 0·80 |
| $Na^{+1}$ . $10^2$ | 322 | 346 | 292 | 147 | 289 | 300 | 304 | 275 | — | 0·97 |
| $Ca^{+2}$ . $10^2$ | 344 | 139 | 63 | 24 | 132 | 51 | 103 | 204 | — | 0·99 |
| $K^{+1}$ . $10^2$ | 161 | 241 | 189 | 304 | 174 | 161 | 184 | 161 | — | 1·33 |
| $Ga^{+3}$ | 20 | 20 | 10 | 20 | 10 | 8 | 10 | 8 | 2 | 0·62 |
| $Cr^{+3}$ | 22 | 41 | 18 | 41 | 22 | 18 | 34 | 27 | 2 | 0·63 |
| $V^{+3}$ | 118 | 118 | 76 | 93 | 84 | 76 | 93 | 84 | 5 | 0·74 |
| $Sn^{+4}$ | * | * | 13 | 13 | 20 | 13 | 13 | 20 | 10 | 0·71 |
| $Li^{+1}$ | 10 | 10 | 25 | 25 | 25 | 25 | 25 | 25 | 1 | 0·68 |
| $Ni^{+2}$ | 8 | 63 | 6 | 10 | 8 | 5 | 8 | 8 | 2 | 0·69 |
| $Co^{+2}$ | 12 | 12 | 4 | 4 | 4 | 4 | 4 | 4 | 3 | 0·72 |
| $Sc^{+3}$ | 8 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 10 | 0·81 |
| $Zr^{+4}$ | 164 | 270 | 230 | 164 | 164 | 164 | 270 | 270 | 10 | 0·79 |
| $Y^{+3}$ | 4 | 11 | 6 | 6 | 6 | 8 | 25 | 6 | 3 | 0·92 |
| $Sr^{+2}$ | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 2 | 1·12 |
| $Pb^{+2}$ | 33 | 72 | 72 | 58 | 48 | 58 | 39 | 39 | 8 | 1·20 |
| $Ba^{+2}$ | 226 | 226 | 226 | 226 | 226 | 226 | 226 | 226 | 5 | 1·34 |
| $Rb^{+1}$ | 50 | * | 50 | 150 | 30 | 50 | * | * | 10 | 1·47 |
| Ga × 1000/Al | 0·20 | 0·21 | 0·13 | 0·19 | 0·13 | 0·11 | 0·12 | 0·09 | | |
| Cr × 100/Ti | 0·48 | 0·79 | 0·62 | 0·89 | 0·55 | 0·64 | 0·85 | 0·58 | | |
| Cr × 1000/Fe | 0·44 | 1·2 | 0·74 | 1·2 | 0·69 | 0·81 | 0·95 | 0·60 | | |
| V × 10/Ti | 0·26 | 0·23 | 0·26 | 0·20 | 0·21 | 0·27 | 0·23 | 0·18 | | |
| V × 100/Fe | 0·24 | 0·34 | 0·31 | 0·26 | 0·26 | 0·34 | 0·26 | 0·19 | | |
| Ni × 100/Ti | 0·17 | 1·2 | 0·21 | 0·22 | 0·20 | 0·18 | 0·20 | 0·17 | | |

† Numbers refer to the profile number, thus 1 = parent material of profile 1.
Å = ionic radii in Å; S = sensitivity. All figures are expressed in ppm., major elements × $10^2$; * = below sensitivity; Be, S = 30; Mo, S = 2; La, S = 30; Ag, S = 0·5; Cs, S = 15 are all *.

in these cases no doubt lie in the varying anorthitic content of the plagioclase. As mentioned previously, veinlets of clinozoisite occurred in one sample (No. 5), and this would deplete the lime content of the remaining rock and give the low value observed. Carbonate, phosphate, and fluoride, although present in some samples, were not determined. The minor elements also presented in the Table will be discussed later.

## Methods of Analysis

The soils collected were prepared for analysis in the standard manner. The northern samples contained no coarse material, whereas those from cooler regions (e.g., profile 7) contained up

to 50 per cent material coarser than sand grade. This is a reflection of the greater efficiency of the weathering processes under warmer climatic conditions.

Mechanical analyses following the standard pipette method (Robinson, 1930) were carried out, but treatment with N/5 hydrochloric acid after the peroxide treatment was omitted, for these same samples were split subsequently into their various fractions, and it was considered that use of strong acid might have effected a change in the chemical composition of the clay.

It should be noted that the errors in working with oven-dry material are mainly positive, and often, in soils of low organic content, outweigh the organic matter dissolved by peroxide. In this case, the total of the sand + silt + clay + moisture will exceed 100, in contrast to the usual experience with ignited material, where the errors are mainly negative and lead to a total of less than 100. In soils of high organic content, such as the humic layer of podzols, the figure quoted for the clay percentage is inaccurate, for, due to the impracticability of destroying all of the organic matter, this material enters into the clay figure. This remark is especially applicable to the surface horizons of the more southern samples.

The various fractions were quantitatively separated by centrifugal means, and the silts and more especially the clays were examined, using chemical, X-ray, differential thermal, and spectrographic analytical techniques.

It has been found advantageous during the final stages of fractional separation to dehydrate the clay fractions gradually, using successively stronger ethyl alcohol, until absolute alcohol may be used. Several final washings with acetone ensure that, on drying, the material may be easily powdered without grinding.

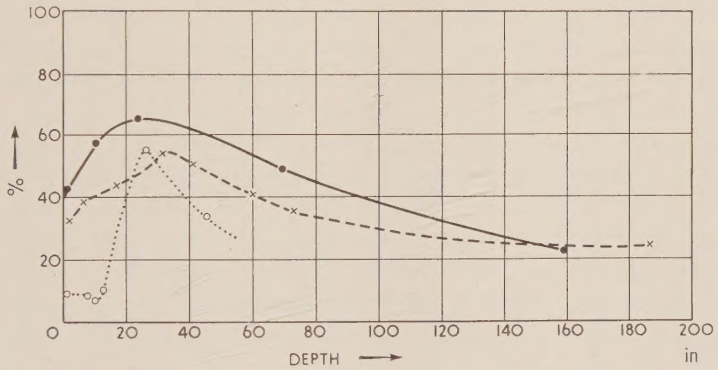


Fig. 1. Clay percentage of profile 1 —— O ——, profile 2 - - - -×- - - -, profile 3- - - - O - - - -

## Results

The results of mechanical analyses are shown in tabular form in Table 2, and may be summarized as follows.

The percentage clay present in the podzolized samples rises rapidly to a maximum in the zone of clay enrichment (the *B* horizon). This rise is always preceded by a drop in percentage in the zone of maximum leaching (the $A_2$ horizon). After the maximum has been reached in the *B* horizon, the amount present immediately falls again. This points to the removal of clay from the surface layers, and deposition in the *B* horizon; an effect noted by numerous other workers (Tamm, 1920; Shaw, 1928). This shifting of clay from higher to lower horizons appears to be able to reach only a certain value, determined no doubt by the climatic conditions obtaining, for in the most northern samples—profiles 1, 2 and 3—the peak clay percentage of the podzol does not exceed that of the immature soil. The effect has been shown in Fig. 1. The organic matter content may be very roughly estimated by adding together sand and silt and clay and moisture

*Table 2. Mechanical analyses results*

| *Number and depth in inches* | *Sand %* | *Silt %* | *Clay %* | *Number and depth in inches* | *Sand %* | *Silt %* | *Clay %* | *Number and depth in inches* | *Sand %* | *Silt %* | *Clay %* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Profile 1 (immature) | | | | Profile 2 (mid semi-mature) | | | | Profile 3 (mature) | | | |
| 0–2 | 14·7 | 33·2 | 42·3 | 0–4 | 26·0 | 34·7 | 32·0 | 0–2 | 38·1 | 50·4 | 7·9 |
| 8–12 | 10·8 | 28·4 | 57·3 | 4–7 | 25·6 | 33·1 | 38·2 | 7–9 | 39·9 | 54·8 | 8·2 |
| 20–26 | 9·6 | 22·3 | 65·1 | 11–22 | 20·5 | 28·7 | 46·3 | 9–11½ | 40·3 | 55·9 | 6·7 |
| 66–72 | 22·8 | 26·9 | 46·8 | 29–32 | 13·0 | 32·1 | 54·0 | 12–14½ | 38·5 | 49·9 | 9·7 |
| 156–162 | 45·9 | 29·9 | 22·6 | 38–44 | 10·3 | 39·7 | 49·9 | 24–28 | 10·4 | 32·9 | 55·3 |
| | | | | 58–61 | 11·5 | 47·3 | 41·1 | 42–48 | 23·7 | 43·0 | 33·0 |
| | | | | 72 | 43·9 | 21·3 | 35·3 | | | | |
| | | | | 180–192 | 50·3 | 25·0 | 24·3 | | | | |
| Profile 4 (immature) | | | | Profile 6 (immature) | | | | Profile 8 (immature) | | | |
| 0–9 | 57·2 | 27·3 | 9·9 | 0–1½ | 38·8 | 23·7 | 26·7 | 0–4 | 51·1 | 28·2 | 13·1 |
| 10–16 | 56·3 | 32·8 | 8·5 | 2–11 | 45·7 | 30·8 | 19·3 | 5–8 | 49·7 | 27·9 | 19·6 |
| 18–24 | 59·3 | 28·2 | 6·7 | 11–15 | 49·7 | 28·2 | 20·0 | 11–16 | 57·2 | 29·8 | 14·0 |
| | | | | 16–21 | 46·7 | 31·1 | 20·8 | 28–33 | 63·5 | 21·8 | 13·8 |
| | | | | 28–32 | 50·9 | 27·6 | 21·9 | | | | |
| Profile 5 (mature) | | | | Profile 7 (mature) | | | | Profile 9 (mature) | | | |
| 0–6 | 25·9 | 21·9 | 5·5 | 0–1 | 1·3 | 5·9 | 17·5 | 0–6 | 1·3 | 8·5 | 32·2 |
| 6–8 | 36·3 | 20·2 | 5·0 | 1–4 | 11·5 | 7·1 | 11·7 | 8–12 | 1·1 | 13·8 | 30·4 |
| 8–12 | 35·0 | 32·8 | 7·0 | 5–7 | 58·7 | 26·4 | 12·8 | 12–18 | 43·1 | 30·0 | 15·9 |
| 12–16 | 42·1 | 36·1 | 8·7 | 10–15 | 51·3 | 25·0 | 18·3 | 20 | N.D. | 30·6 | 19·6 |
| 40–44 | 53·7 | 35·1 | 5·6 | 30–32 | 75·2 | 15·9 | 8·9 | 20–26 | 45·8 | 36·0 | 11·9 |

and deducting from 100. This would indicate that, with an increase in annual temperature, the amount of organic matter in the soil falls, due to more rapid decomposition of the humus.

Combining the clay data with climatic data, it is apparent that increase in annual temperature causes a rapid rise in the percentage of clay present. No conclusive evidence has been drawn from the effect of annual rainfall. The findings are in accord with those of others (Brown and Byers, 1935; Coffey, 1912; Jenny, 1941; Thorpe, 1931).

Selected clay fractions were analyzed by X-ray diffraction using the powder method, 9 cm camera, and iron target with penterithritol monochromator. The lines remaining after accounting for quartz and kaolinite have been accounted for as haematite—2·68 Å (*circa*) and 1·70 Å (the 2·51 Å is probably obscured by the 2·49-Å kaolinite line); anatase—enhancement of 1·89-Å kaolinite line, and probably also the 1·70-Å haematite line (the strongest anatase line varies in position and is probably concealed by the 3·57-Å strong kaolinite line); hydrous-mica mineral—10·0 Å (*circa*); 4·9 Å; 3·20 Å; 3·00 Å; 2·87 Å; 2·80 Å; 1·50 Å. Feldspar—6·3 Å; 4·04 Å; 3·78 Å; 3·70 Å; 3·20 Å.

It has been observed that the tendency towards crystallinity is enhanced by a rise in mean annual temperature, for in the northern samples, i.e., profiles 1, 2, and 3, not only does the iron oxide become crystalline, as haematite, but also the powder pattern for kaolinite is much clearer than those of specimens from colder regions, for in these the lines are blurred and displaced towards higher spacings at low angles. In direct contrast to this is the interesting effect observed in the case of the hydrous mica mineral. In profile 7, which, due to its altitude, suffers quite severe winters, the mineral is a slightly hydrated muscovite. In profiles where the annual temperature is higher, the amount of this mineral decreases rapidly and is replaced by a mineral of illitic nature whose diffraction pattern is rather broad and indeterminate. In no case was montmorillonite found, and this perhaps is to be expected, for acid conditions and free-leaching obtain (Ross, 1943). The hydrous-mica mineral is dioctahedral in nature as judged by the spacing at 1·50 Å (Walker, 1950), again as one might expect if its genesis is from a sericitic decomposition product of feldspar. No hydrous mica occurred in profiles 1, 2, and 3, with the exception of the two deepest horizons of profile 2, and this will be discussed later.

By investigation with differential thermal analysis, some interesting quantitative data were obtained. The standardization of the instrument, and the proof of the validity of correlating area under endothermic curve with percentage mineral present, finds substantiation in X-ray and chemical analyses and has been published in detail elsewhere (McLaughlin, 1954). The results are tabulated in Table 3. The values for kaolinite obtained for profiles 1–3 inclusive are accurate, for here X-ray, chemical, and differential thermal methods of analysis are in good agreement. The values obtained for the remaining series are open to doubt, for in these there is admixture of varying amounts of a hydrous mica of illitic composition. No allowance has been made for this material, and as it has an endothermic peak in the same region as the kaolinitic peak, the areas obtained by planimeter readings include the effect of the illitic material. As the endothermic

*Table 3. Differential thermal analysis results*

*A—CLAYS*

| *Depth in inches* | *Averaged area of endothermic peak corrected to constant weight* | *Averaged temp. of peak (°C)* | *Curve type* | *Kaolinite %* | *Depth in inches* | *Averaged area of endothermic peak corrected to constant weight* | *Averaged temp. of peak (°C)* | *Curve type* | *Kaolinite %* |
|---|---|---|---|---|---|---|---|---|---|
| Profile 1 | | | | | Profile 5 | | | | |
| 0–2 | 22·4 | 571 | 1 | *63* | 0–6 | N.D. | 507 | 3 | N.D. |
| 8–12 | 20·6 | 571 | 1 | *61* | 6–8 | N.D. | 532 | 3 | N.D. |
| 20–26 | 20·7 | 572 | 1 | *58* | 8–12 | N.D. | 542 | 3 | N.D. |
| 66–72 | 23·2 | 583 | 1 | *69* | 12–16 | 9·4 | 562 | 2 | 28 |
| 156–162 | 27·0 | 579 | 1 | *72* | 40–44 | 5·9 | 535 | 2 | 18 |
| Profile 2 | | | | | Profile 6 | | | | |
| 0–4 | 26·5 | 586 | 1 | *74* | 0–1½ | N.D. | 544 | 4 | N.D. |
| 4–7 | 26·6 | 589 | 1 | 74 | 2–11 | 11·7 | 548 | 2 | 36 |
| 11–22 | 27·2 | 582 | 5 | 75 | 11–15 | 14·1 | 544 | 2 | 43 |
| 29–32 | 27·3 | 583 | 5 | *73* | 16–21 | 14·8 | 540 | 2 | 44 |
| 39–44 | 31·1 | 583 | 1 | 84 | 28–32 | 19·3 | 536 | 2 | 57 |
| 58–61 | 28·1 | 578 | 6 | 76 | Profile 7 | | | | |
| 72 | N.D. | N.D. | 6 | N.D. | 1–4 | N.D. | 535 | 3 | N.D. |
| 180–192 | N.D. | N.D. | 6 | N.D. | 5–7 | 6·4 | 546 | 3 | 20 |
| Profile 3 | | | | | 10–15 | 1·6 | 525 | 8 | 5 |
| 0–6 | 12·8 | 547 | 3 | *20* | 30–32 | 3·5 | 503 | 2 | 11 |
| 7–9 | 9·8 | 547 | 3 | *32* | Profile 8 | | | | |
| 9–11½ | N.D. | 547 | 3 | *31* | 0–4 | 11·0 | 544 | 2 | 34 |
| 12–14½ | 16·9 | 550 | 2 | *55* | 5–8 | 17·7 | 544 | 2 | 54 |
| 24–28 | 26·0 | 575 | 2 | *72* | 11–16 | 13·2 | 546 | 2 | 40 |
| 42–48 | 28·0 | 581 | 1 | *76* | 28–33 | 11·4 | 549 | 2 | 35 |
| Profile 4 | | | | | Profile 9 | | | | |
| 0–9 | 4·5 | 527 | 3 | 14 | 0–6 | N.D. | N.D. | 4 | N.D. |
| 10–16 | 4·0 | 533 | 3 | 13 | 8–12 | N.D. | N.D. | 4 | N.D. |
| 18–24 | 4·0 | 535 | 3 | 13 | 12–18 | 21·4 | 549 | 2 | 62 |
| | | | | | 20–26 | 17·4 | 554 | 2 | 53 |

*B—SILTS*

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Profile 1 | | | | | Profile 5 | | | | |
| 0–2 | 11·4 | 540* | 7 | *26·7* | 0–6 | N.D. | N.D. | 4 | N.D. |
| 8–12 | 6·5 | 540* | 7 | *17·9* | 6–8 | N.D. | 570 | 4 | N.D. |
| 20–26 | 9·9 | 547* | 7 | *27·1* | 8–12 | N.D. | 580 | 4 | N.D. |
| 66–72 | 27·8 | 565 | 1 | *61·5* | 12–16 | 3·2 | 515* | 8 | 8 |
| 156–162 | 26·6 | 565 | 1 | *64·7* | 40–44 | 2·0 | 515* | 9 | 5 |
| Profile 3 | | | | | Profile 8 | | | | |
| 0–6 | 1·2 | 498* | 9 | *1·3* | 0–4 | 11·4 | 542* | 8 | 27 |
| 7–9 | 0.9 | 498* | 9 | *1·5* | 5–8 | 10·6 | 542* | 8 | 25 |
| 9–11½ | 1·6 | 498* | 9 | *2·0* | 11–16 | 7·5 | 547* | 8 | 17 |
| 12–14½ | 3·2 | 521* | 9 | *6·5* | 28–33 | 6·5 | 542* | 7 | 15 |
| 24–28 | 30·4 | 572 | 1 | *76·7* | Profile 9 | | | | |
| 42–48 | 35·0 | 575 | 1 | *77·4* | 0–6 | N.D. | N.D. | 4 | N.D. |
| Profile 4 | | | | | 8–12 | N.D. | N.D. | 4 | N.D. |
| 0–9 | 0·7 | 583 | 4 | 1 | 12–18 | N.D. | N.D. | 4 | N.D. |
| 10–16 | 2·1 | 521* | 9 | 4·8 | 20–26 | 7·5 | 542* | 7 | 17 |
| 18–24 | 2·1 | 515* | 8 | 4·8 | | | | | |

Kaolinite % values italicized derived from chemical analyses.
* Subsidiary peak due to quartz.

heat effect is comparatively small when considered in relation to kaolinite, and as in only a few cases did the amount present reach large proportions, as judged from X-ray powder photographs, the error introduced is probably not large and in many cases is offset by the exothermic reaction due to organic matter. In some samples even 100-volume hydrogen peroxide would not remove all the organic matter, and this appears in the clay and silt fractions. The exothermic reaction due to oxidation of this material often masks completely the endothermic reactions due to

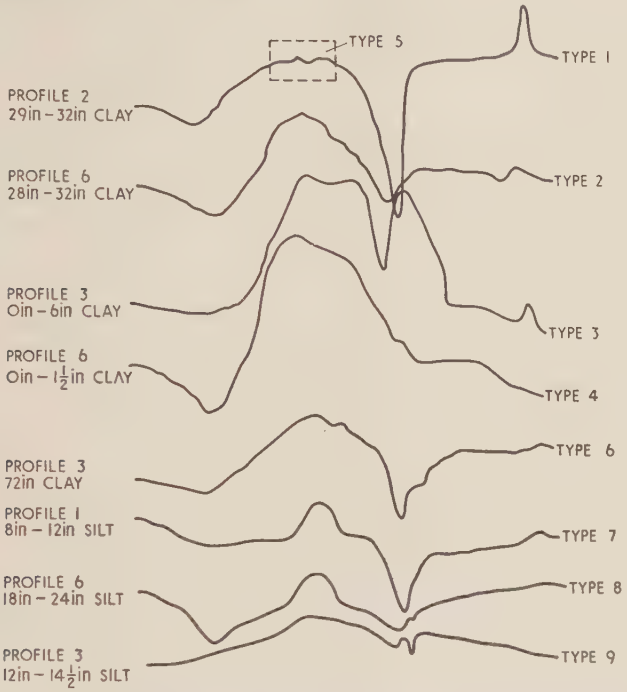


Fig. 2. Types of differential thermal curves. For explanation see text.

kaolinite + illite, and in some rare cases the effect due to the clay minerals is impressed across the top of the exothermic reaction. For this reason values for some surface horizons are not given. There is a marked tendency for peak temperature to increase with peak area, and this can be used as a preliminary estimate of amount of reactive material present. The exothermic peaks have not been used for any quantitative data, for these are subject to great fluctuations in area and position with content of iron oxide and/or alkali of the sample (Caillère and Hénin, 1947; Grim and Rowland, 1942; Saunders and Giedroyc, 1950). Furthermore, the presence of illitic material complicates the matter, for often there are double peaks. Many samples, especially those which had pronounced caking (often of a brick-like nature), after heating in the apparatus, show small endothermic peaks in the 350°C and 290°C region (Fig. 2, type 5). These quite probably represent an iron oxide mineral. As the area of the endothermic peak due to kaolinite falls, the peak due to the quartz inversion can be distinguished, first as a slight indention on the up-slope of the kaolinite peak. With a smaller percentage of kaolinite it

becomes more visible and eventually at very low percentages two separate peaks are observed. (Fig. 2, types 7, 8, and 9.)

In the calculation of clay mineral percentages for silts and clays, separate graphs have been used, for larger grain size necessarily means larger peak area for similar weights of material under similar conditions (Speil and Berkelhamer, 1945; McLaughlin, 1954). The column in Table 3 containing the curve type relates the sample to the closest representative in Fig. 2, where the various types of curve have been drawn. Curve type No. 6 occurs only in the two deepest horizons of profile 2. From X-ray powder diagrams the material contains a hydrous mica of illitic nature. Because the content is higher in the sample at 72 in. than at 180 to 192 in., it seems that the material represents a concentration of clay mineral washed down the profile. In a soil profile, not described in this paper, material has been collected from drainage channels caused by soil shrinkage, and this material gives exactly the same type of differential thermal analysis and X-ray pattern; hence the origin by leaching from above seems quite applicable to the case of profile 2 in the deeper horizons, for similar drainage channels occur in this profile

Experiments on removal of free iron oxides with ammonium tartrate and aluminium foil by the Dion (1944) method have shown that the resultant samples suffered little change when the hydrous mica was absent, except where the clay content was increased by de-cementation of aggregates with individual particles less than two microns, and in these an increase in area of endothermic peak corresponds to the increase of clay mineral introduced, i.e., the cemented material was kaolinitic. In samples containing moderate amounts of the hydrous mica there was often a decrease in area of endothermic peak, and it seems therefore that the iron removal process also attacks the hydrous mica.

The percentages of kaolinite obtained by differential thermal analysis have been plotted against depth for several profiles, and appear in Figs. 3, 4, 5, and 6. The values for profiles, 1, 2, and 3 are accurate to $\pm 5$ per cent, for these samples were used as their own standards when constructing area of endothermic peak against percentage of kaolinite graphs. The values for other profiles are not so accurate, due to the admixture of the hydrous mica in varying proportions. The following conclusions may be drawn from Figs. 3, 4, 5, and 6, and Table 3. For profiles not strongly weathered, the surface horizons may contain more kaolinite than the horizons immediately beneath, and this mineral is evidently held by the action of the humus material. Furthermore, it has been observed that the breakdown of kaolinite may be delayed until the 700°C region, in materials (especially silts) very rich in organic matter. For profiles 1–3 inclusive and profile 6 the amount of kaolinite increases after the leached horizon has been passed, and keeps on increasing even after the *B* horizon. Therefore the depth : percentage kaolinite of clay fraction graphs (Figs. 3 and 4) differ quite markedly from depth : percentage clay curves. This is an interesting observation, for it would mean that the processes responsible for formation of this clay mineral are merely leaching solutions, while the part played by the uppermost layers of the soil is degradational. A comparison of Figs. 3 and 4 shows that the podzolized sample contains little kaolinite except at depth, and furthermore, more under the clay

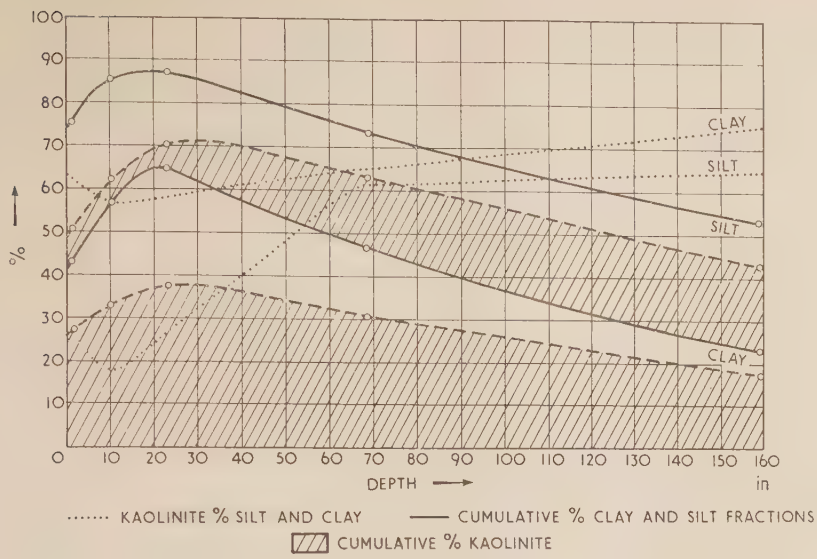


Fig. 3. Kaolinite percentages in profile 1.

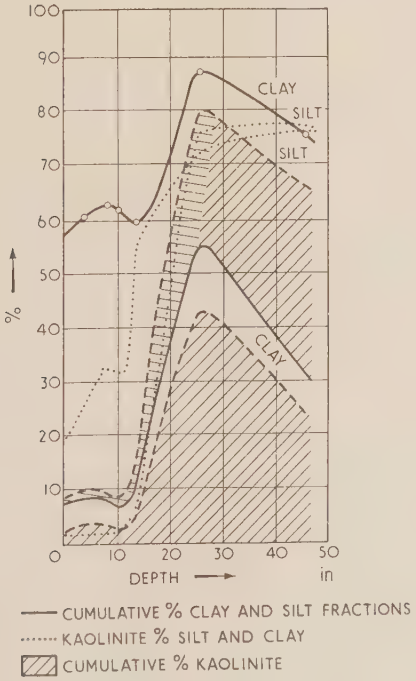


Fig. 4. Kaolinite percentage of profile 3.

pan than in it. It is infortunate that no deeper horizons were collected for this profile, but it seems quite likely from the field evidence that the lower horizons would act in a similar fashion to those of profile 1. While the deep weathering of these northern samples may be in part due to their being weathered whilst glaciation was taking place further south, the existence of the same phenomenon of rise in the percentage of kaolinite with depth, in profile 6 (Fig. 5), a locality

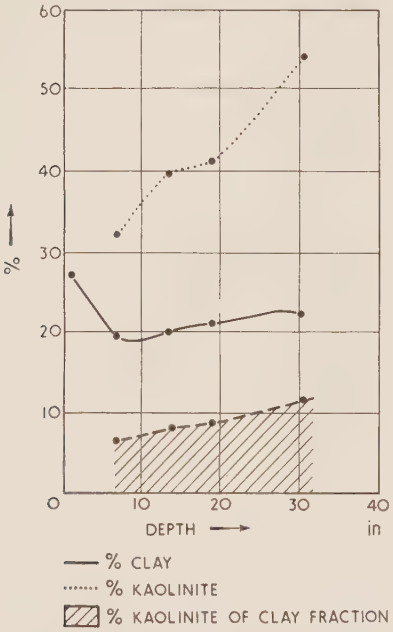


Fig. 5. Kaolinite percentage in profile 6.

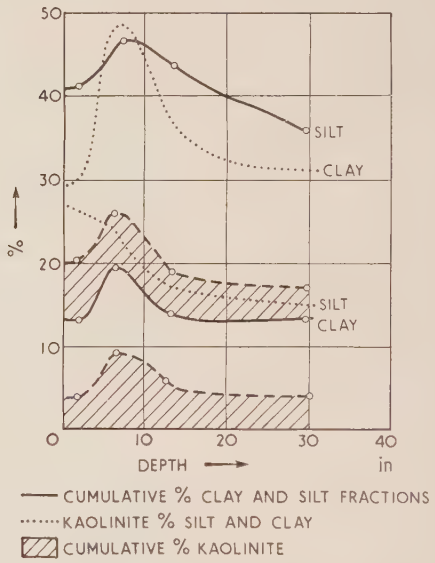


Fig. 6. Kaolinite percentage in profile 8.

most certainly glaciated, precludes any explanation of the observed facts by any theory based solely on extra-glacial weathering. The effect of increasing soil maturity is to lower the clay mineral percentage in surface horizons, but little effect is felt at depth. This is further supported by the increase of kaolinite with depth in the silt fractions of such mature profiles, until the amount exceeds that present in the clay. That this is not a cementing effect has been investigated by free $R_2O_3$ removal by various methods (Dion, 1944; Galabutskaya and Govorova, 1934), and the low contents of iron oxide in the silt fractions (Table 4) forbid any such conclusion.

The effect of increasing annual temperature is to increase the rapidity with which the formation of kaolinite takes place, and eventually all micaceous products of weathering are completely converted to kaolinite. In profiles formed under cooler conditions, the hydrous mica increases and, as pointed out previously, so too does unweathered micaceous material, probably sericitic in nature.

In those profiles formed under cooler conditions there is a decrease in clay mineral content with depth (see profiles 4, 5, 7, 8, and 9, and Fig. 6). In fact the percentage kaolinite curve behaves sympathetically with the percentage clay curve. No quantitive data are available as regards relative amounts of kaolinite and hydrous mica.

## Variations of Major and Minor Elements

Chemical analyses of selected samples are presented in Table 4. Various relationships between the elements have been calculated and are presented in the table. Estimations of the minor elements were semi-quantitative, and the method used was similar to that described by Nockolds and Allen (1953), with the exception that the standards were prepared mixtures in which composition corresponded to average composition of silts and clays.

Referring to Table 4, silicon is accumulated in silts relative to clays, and the effect is more apparent in the podzolized sample (profile 3). The behaviour of aluminium is to increase with depth, while strong leaching causes a greater disparity between the values for silts and those for clays. Combining the two effects, the silicon/aluminium ratios are higher for silts than clays in surface layers, increasing with leaching efficacy. At depth the ratios approach each other, this depth being shallower for the podzol. The values show in an interesting fashion the conclusion reached by mineralogical analysis, that the zone of clay concentration (Table 2) is not accumulation of a clay mineral, but relative accumulation of silica with respect to the horizons beneath.

The tendency of titanium to rise in concentration with depth due to immature weathering is reversed in the clays of the podzol. The silts show minor alteration when compared with the parent material, but with the clays, concentration factors varying between 2 and 5 occur, the highest being in the podzol and in the surface layers. The two effects are simply explained. Accumulation of Ti in lower layers is a reflection of the resistance of the titaniferous magnetite to weathering when compared with the other primary minerals. Strong concentration in clays of the podzol is due to solution of titanium from its parent mineral, and almost immediate precipitation of the oxide on clay particles, an effect rendered very easy by the high charge density on the $Ti^{4+}$ ion and insolubility of $Ti^{4+}$ ions in the conditions operative. If any attempt is made to explain this accumulation as due to insolubility of Ti-bearing minerals, the silts also should show a high Ti content, and such is not found to be the case. The Ti appears to travel to the oxide via a hydrated oxide (cf. Mellor, 1927), or it would be difficult to explain the ease with which some titanium may be removed from the clays. The most decisive argument is the appearance of lines due to anatase in X-ray photographs of these clays, and there is certainly no trace of this in the parent material.

The values shown for ferric iron represents total iron, for ferrous iron determinations would be meaningless in view of the previous use of hydrogen peroxide. The iron is concentrated preferentially in the clays, but differences in values between silts and clays tend to disappear at depth, and hence the aluminium/ferric iron ratios show a crossing over at depth when silts and clays are compared. It is possible to explain the behaviour of iron in terms of those just applied to titanium. There is an increase with depth if leaching is not severe, merely due to relative stability of the iron-bearing minerals, aided also no doubt by some precipitation of ferric oxide. Under podzolizing conditions there is mobilization of the iron and precipitation at depth in the iron-pan at 12 to 14½ in. and also about the clay mineral grains, hence higher values for clays than silts.

*Table 4. Major and minor elements in profiles 1 and 3.*

Profile 1

| † | *Silts* | | | | | *Clays* | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0–2 | 8–12 | 20–26 | 66–72 | 156–162 | 0–2 | 8–12 | 20–26 | 66–72 | 156–162 | Arkose 192 |
| $Si^{+4} \times 10^2$ | 3340 | 3767 | 3518 | 2470 | 2265 | 2154 | 2253 | 2194 | 1923 | 1914 | 2699 |
| $Al^{+3} \times 10^2$ | 557 | 374 | 567 | 1286 | 1353 | 1327 | 1285 | 1217 | 1445 | 1500 | 1025 |
| $Ti^{+4} \times 10^2$ | 40 | 44 | 44 | 67 | 78 | 100 | 87 | 162 | 78 | 90 | 46 |
| $Fe^{+3} \times 10^2$ | 365 | 295 | 393 | 574 | 615 | 678 | 684 | 876 | 902 | 771 | 494 |
| $Mg^{+2} \times 10^2$ | 14 | 18 | 12 | 17 | 7 | 76 | 43 | 42 | 13 | — | 38 |
| $Mn^{+2} \times 10^2$ | 3 | 1 | 1 | 1 | 1 | 5 | 1 | 4 | 1 | 5 | 7 |
| $Na^{+1} \times 10^2$ | 18 | 20 | 15 | 8 | 10 | 6 | 7 | 3 | 7 | 2 | 322 |
| $Ca^{+2} \times 10^2$ | 46 | 42 | 25 | 40 | 11 | 37 | 22 | 43 | 6 | 21 | 344 |
| $K^{+1} \times 10^2$ | 40 | 31 | 30 | 25 | 40 | 80 | 56 | 34 | 11 | 28 | 161 |
| $Ga^{+3}$ | 8 | 4 | 4 | 10 | 10 | 10 | 10 | 8 | 4 | 8 | 20 |
| $Cr^{+3}$ | 18 | 10 | 10 | 10 | 18 | 10 | 18 | 18 | 10 | 10 | 22 |
| $V^{+3}$ | 125 | 125 | 125 | 90 | 171 | 125 | 171 | 90 | 171 | 171 | 118 |
| $Sn^{+4}$ | T | 13 | T | T | T | * | * | * | * | * | * |
| $Li^{+1}$ | 17 | 17 | 11 | 11 | 11 | 17 | 17 | 11 | 7 | 11 | 10 |
| $Ni^{+2}$ | 10 | 5 | 7 | 10 | 10 | 7 | 10 | 7 | 4 | 7 | 8 |
| $Co^{+2}$ | 6 | * | * | * | 15 | 4 | 4 | 4 | 4 | 6 | 12 |
| $Sc^{+3}$ | * | * | * | * | * | * | * | * | * | * | 8 |
| $Zr^{+4}$ | 100 | 100 | 164 | 100 | 164 | 100 | 164 | 164 | 164 | 164 | 164 |
| $Y^{+3}$ | T | T | T | T | 20 | 3 | 3 | 3 | 12 | 12 | 4 |
| $La^{+3}$ | * | * | * | * | * | * | * | * | * | * | * |
| $Sr^{+2}$ | >173 | 173 | 173 | 173 | 173 | 32 | 32 | — | 173 | 3 | 100 |
| $Pb^{+2}$ | 58 | 32 | 58 | 6 | 18 | 32 | 32 | 32 | 32 | 32 | 32 |
| $Ba^{+2}$ | 104 | 104 | 104 | 62 | 160 | 62 | 62 | — | 62 | 32 | 226 |
| $Rb^{+1}$ | 10 | 6 | 8 | 6 | 30 | 65 | 30 | — | 10 | 30 | 50 |
| Si/Al | 5·99 | 10·07 | 6·21 | 1·92 | 1·67 | 1·62 | 1·75 | 1·80 | 1·33 | 1·28 | 2·63 |
| Al/Fe | 1·53 | 1·27 | 1·44 | 2·24 | 2·20 | 1·96 | 1·88 | 1·39 | 1·60 | 1·95 | 2·08 |
| K + Na/Al | 0·104 | 0·136 | 0·079 | 0·026 | 0·038 | 0·065 | 0·049 | 0·030 | 0·012 | 0·020 | 0·471 |
| K/Na | 2·22 | 1·55 | 2·00 | 3·13 | 4·0 | 13·3 | 8·00 | 11·3 | 1·57 | 14·0 | 0·50 |
| Ga × 1000/Al | 0·14 | 0·11 | 0·07 | 0·08 | 0·07 | 0·08 | 0·08 | 0·07 | 0·03 | 0·05 | 0·20 |
| Cr × 100/Ti | 0·45 | 0·23 | 0·23 | 0·15 | 0·23 | 0·10 | 0·21 | 0·11 | 0·13 | 0·11 | 0·48 |
| V × 10/Ti | 0·31 | 0·28 | 0·28 | 0·13 | 0·22 | 0·13 | 0·19 | 0·06 | 0·22 | 0·19 | 0·26 |
| V × 100/Fe | 0·34 | 0·42 | 0·32 | 0·16 | 0·28 | 0·18 | 0·25 | 0·10 | 0·19 | 0·22 | 0·24 |
| Sr × 10/Ca | >0·38 | 0·41 | 0·69 | 0·43 | 1·6 | 0·87 | 0·15 | — | 2·9 | 0·01 | 0·03 |
| Ba × 10/Ca | 0·23 | 0·25 | 0·42 | 0·15 | 1·5 | 0·17 | 0·28 | — | 1·0 | 0·15 | 0·07 |
| Ign. loss % | 10·14 | 6·04 | 6·68 | 12·54 | 14·26 | 15·20 | 14·23 | 13·72 | 16·10 | 16·82 | 2·05 |

Profile 3

| *Silts* | | | | | | *Clays* | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0–6 | 7–9 | 9–11½ | 12–14½ | 24–28 | 42–48 | 0–6 | 7–9 | 9–11½ | 12–14½ | 24–28 | 42–48 | *S* | *A* |
| 4481 | 4525 | 4535 | 4251 | 2322 | 2266 | 3644 | 3288 | 3400 | 1773 | 1709 | 1987 | — | 0·42 |
| 26 | 32 | 41 | 135 | 1603 | 1617 | 424 | 671 | 656 | 1143 | 1527 | 1577 | — | 0·51 |
| 44 | 29 | 39 | 38 | 25 | 53 | 132 | 251 | 228 | 164 | 100 | 77 | — | 0·68 |
| 20 | 22 | 24 | 220 | 410 | 405 | 91 | 104 | 122 | 1276 | 1004 | 592 | — | 0·64 |
| 5 | 5 | 6 | 8 | 4 | 8 | 57 | 12 | 8 | 18 | 10 | 8 | — | 0·66 |
| <1 | <1 | <1 | <1 | <1 | <1 | 1 | 1 | 1 | 1 | 1 | T | — | 0·80 |
| 13 | 7 | 10 | 6 | 12 | 17 | 25 | 5 | 7 | 13 | 19 | 21 | — | 0·97 |
| 21 | 24 | 16 | 19 | 9 | 8 | 13 | 21 | 11 | 32 | 16 | 4 | — | 0·99 |
| 16 | 7 | 12 | 6 | 55 | 60 | 21 | 15 | 14 | 17 | 135 | 295 | — | 1·33 |
| 4 | * | * | 4 | 8 | 10 | 4 | 10 | 10 | — | 8 | 10 | 2 | 0·62 |
| 5 | 5 | 3 | 5 | 10 | 27 | 7 | 10 | 10 | 10 | 18 | 41 | 2 | 0·63 |
| * | * | T | 45 | 90 | 125 | 90 | 171 | 171 | 171 | 125 | 125 | 5 | 0·74 |
| 20 | 20 | T | T | * | * | 67 | 46 | T | * | * | * | 10 | 0·71 |
| 11 | 11 | 17 | 11 | 17 | 17 | 7 | 11 | 11 | 17 | 28 | 17 | 1 | 0·68 |
| 4 | 4 | 4 | 5 | 7 | 7 | 4 | 10 | 7 | 7 | 7 | 5 | 2 | 0·69 |
| 4 | 4 | 6 | 4 | 4 | 4 | * | * | * | * | * | * | 3 | 0·72 |
| * | * | * | * | * | * | * | * | * | * | * | * | 8 | 0·81 |
| 450 | 450 | 450 | 330 | 164 | 164 | 330 | 450 | 450 | 330 | 100 | 164 | 10 | 0·79 |
| T | * | 3 | * | * | * | 31 | 31 | 46 | 23 | * | 3 | 3 | 0·92 |
| * | * | * | * | * | * | 32 | 18 | 13 | — | * | 100 | 13 | 1·14 |
| 6 | 32 | 18 | 173 | 100 | 100 | 32 | 32 | 100 | 32 | 18 | 18 | 2 | 1·12 |
| 10 | * | 10 | 32 | 32 | 32 | 32 | 100 | 32 | 32 | 32 | 58 | 6 | 1·20 |
| 32 | 62 | 104 | 62 | 104 | 160 | 160 | 160 | 104 | 104 | 62 | 160 | 5 | 1·34 |
| 6 | 6 | 6 | 6 | 30 | 100 | 6 | 6 | 30 | 65 | 106 | 200 | 5 | 1·47 |
| 172 | 141 | 111 | 31·4 | 1·45 | 1·40 | 8·59 | 4·90 | 5·18 | 1·55 | 1·12 | 1·26 | | |
| 1·30 | 1·45 | 1·71 | 0·61 | 3·91 | 3·99 | 4·66 | 6·45 | 5·38 | 0·90 | 1·52 | 2·66 | | |
| 1·12 | 0·438 | 0.537 | 0·088 | 0·042 | 0·048 | 0·108 | 0·030 | 0·032 | 0·026 | 0·101 | 0·200 | | |
| 1·23 | 1·00 | 1·20 | 1·00 | 4·58 | 3·53 | 0·84 | 3·00 | 2·00 | 1·31 | 7·11 | 14·0 | | |
| 1·5 | <0·63 | <0·49 | 0·30 | 0·05 | 0·06 | 0·09 | 0·15 | 0·15 | — | 0·05 | 0·06 | | |
| 0·11 | 0·17 | 0·08 | 0·13 | 0·40 | 0·51 | 0·05 | 0·04 | 0·04 | 0·06 | 0·18 | 0·53 | | |
| * | * | * | 0·12 | 0·36 | 0·24 | 0·07 | 0·07 | 0·08 | 0·10 | 0·13 | 0·16 | | |
| * | * | * | 0·20 | 0·22 | 0·31 | 0·99 | 1·6 | 1·4 | 0·13 | 0·12 | 0·21 | | |
| 0·03 | 0·13 | 0·11 | 0·91 | 1·1 | 1·3 | 0·25 | 0·15 | 0·91 | 0·10 | 0·11 | 0·45 | | |
| 0·15 | 0·26 | 0·65 | 0·33 | 1·2 | 2·0 | 1·2 | 0·76 | 0·94 | 0·33 | 0·39 | 4·0 | | |
| 1·43 | 0·87 | 0·80 | 2·36 | 13·45 | 12·85 | 8·75 | 10·80 | 8·90 | 18·40 | 15·80 | 13·60 | | |

† Samples are expressed as depths in inches below surface.
S = sensitivity; A = ionic radii in Å; values are in p.p.m., major elements × $10^2$.
* = below sensitivity; T = trace; — = absence of data.
$Be^{+2}$, S = 30; $Mo^{+4}$, S = 2; Ag, S = 0·5; $Cs^{+1}$, S = 15; all *.

In any competition between $Ti^{4+}$ and $Fe^{3+}$ for adsorption the $Ti^{4+}$ would be much more strongly adsorbed due to its greater charge density; therefore, the iron would travel to a lower level before any such adsorption could take place, and this is exactly what is observed in the figures of Table 4.

Magnesium is concentrated in clays relative to silts and is lost on strong leaching; moreover, the values are always highest for surface layers and quite unrelated to kaolinite content, or there would be a rise with depth. If this element were present in undecomposed biotite or chlorite (the eventual Mg source in the parent material), then it would be expected to concentrate at depth and also in the silt fractions; this is not the case, and hence concentration must be effected by plant material for which Mg is a necessary constituent, and it must be held as a complex organic compound. Manganese behaves in a similar fashion to magnesium, but there is a greater loss due to leaching. The mechanism of transfer is simple, for under aerobic conditions Mn is held (at the surface) and under anaerobic conditions it is readily leached. A low pH also helps leaching, hence the small values for the podzol (Goldschmidt, 1954). Sodium is readily lost during leaching processes, hence clays are lower than silts in their Na content. The figures demonstrate some slight concentration in the surface, doubtless due to plant material. Similarly, calcium shows considerable leaching.

Potassium shows two distinct concentrating factors at work: accumulation in surface layers due to its place in the metabolism of plants, and concentration at depth due to absorption of the relatively large $K^+$ ion on the kaolinite lattice. Strong leaching renders much $K^+$ available, hence strong enrichment occurs in the deeper horizons of the podzol and at a greater depth than the iron, due to the lower charge density of $K^+$. The alkalis/alumina ratios have been calculated to demonstrate the less leached nature of the silt when compared with clay, but the strong potassium enrichment in clays of lower layers of the podzol gives a reversal. The potassium/sodium ratios have been calculated to demonstrate the loss of sodium relative to potassium due to the large ionic size of the latter. These various ratios which have been calculated readily exhibit the effects of podzolization, in the inflexions which occur in their trends, with increasing maturity. It is interesting to observe that these variations are best exhibited by the silt fractions and not by the clays, due to the constant attack the coarser fractions are experiencing.

Before the discussion of the minor elements in the soils, the variation in parent material must be considered. The major constituents have already been discussed and appear in Table 1. It was concluded that there was no great variation between samples. The minor elements of these rocks appear in Table 1, and also in Tables 4 and 5, where their repetition permits ready comparison with silts and clays. The variation between samples is in only a few cases greater than a factor of 2, which is a small variation when the semi-quantitative nature of the method is considered. There are two figures which fall well outside the average values; 63 p.p.m. Ni in No. 2 parent material (no values obtained for clays and silts of this profile), and 25 p.p.m. Y in No. 8. The nickel figure is much higher than any of the other values, but so too is the Ti content of this rock (Table 1). To carry the analogy further, No. 7 with lowest Ti content also has the lowest Ni

content. The corresponding ionic radii have permitted $Ni^{2+}$ to substitute for $Ti^{4+}$ and the main source is probably the titaniferous magnetite. There is no apparent relation between Fe and Ni contents. The cause of the variation of Y in No. 8 is unknown. Comment must be made on the Rb content of No. 5. This sample is the specimen which showed veinlets of clinozoisite due to leaching, and is more weathered than the other specimens, hence not only Rb is high but also the K content.

For comparative purposes, the figures derived for trace elements have been divided into two tables, and the material which has had major constituents also determined is dealt with in more detail. It will be shown later that the other results agree substantially with those trends which may be shown for profiles 1 and 3. In effect the discussion which follows shows the effects of maturity, i.e., stronger leaching, on the movements of the minor constituents. Referring to Table 4, the elements Be, Mo, Ag, and Cs are below sensitivity for all specimens, but Sc appears in the parent materials and not in the clays and silts. This element is evidently easily lost during leaching purposes. Gallium varies sympathetically with Al. It would seem that kaolinite derived by leaching may have a variable Ga/Al ratio and the mechanism may be associated with organic matter; for it is known that Ga accumulates in certain coal ashes (Goldschmidt, 1954) and the Ga $\times$ 1000/Al ratios show that there is a relative concentration of Ga in surface horizons even though, as Butler (1953) has also shown, Ga is lost relative to Al during weathering in lower horizons. Chromium is more closely related to Ti in the parent material than to either Mg or Fe, as ratios between these elements show; the source therefore is the titaniferous magnetite. The Cr $\times$ 100/Ti ratios lie between lower limits for silts and clays than in the parent material, and these two elements have parted during weathering. Considerable leaching is needed before the actual concentration of Cr alters greatly from that of the parent material, and there is concentration in the lower horizons (cf. Robinson, 1914).

Vanadium shows in the parent material strong associations with both Fe and Ti, all three being of rather similar ionic radius, and evidently therefore V occurs in both titaniferous magnetite and biotite. The association V/Fe is stronger than the Cr/Fe ratio (No. 9 parent material is an exception for both Cr and V, and here these two elements must have some other source, perhaps some sphene). On leaching, the ratios V $\times$ 100/Fe show strong relative concentration of V, whereas any association with Ti is obscured, due to actual Ti concentration.

Tin, probably substituting for Mg in the parent material, is concentrated to an even stronger extent than its host during weathering, in the surface horizons. Butler (1954) and Pelisek (1942) have also noted this concentration due to organic matter, and here it is seen to be greater in clays than silts, and increases with leaching efficacy.

Lithium is slightly concentrated in surface horizons if leaching is not strong, but generally there is loss of Li from the profile and, unlike most elements, no concentration at depth.

The relation between Ni and Ti has been discussed previously for the arkoses. There is no apparent relation between Ni and Mg for either arkoses or silts or clays,

which is rather surprising in view of the normal replacement of these elements. The Ti-Ni relationship disappears during weathering; for Ti increases, whereas Ni remains almost constant, dropping in value with stronger leaching.

Cobalt, already very low in content in the parent material, is lost during weathering, an important factor perhaps in the cause of cobalt deficiency diseases.

Zirconium, present in the accessory mineral zircon in the arkose, is concentrated during strong weathering in surface horizons, but in the less leached profile there is a higher amount at depth. The Zr content is the same for both silts and clays, and while the increase of Zr with strong leaching may be explained as due to the great stability of zircon to weathering, it must also be borne in mind that a process similar to that for Ti may also be operative here. The concentration in clay as well as the silt fraction rather suggests this latter hypothesis, as also does the behaviour of the rare-earth elements Y and La; for if, as seems reasonable, these elements are contained in the zircon, then the separation, by concentration in the clay fraction relative to silts under strong weathering of Y and La, is indicative of a break-down of the zircon structure and precipitation on the clay mineral particles.

Strontium is usually related to Ca in its behaviour and while this may be true in the parent materials the Sr $\times$ 10/Ca ratios in silts and clays are very haphazard and prohibit any parallelism. The element is concentrated at depth probably due to adsorption on the clay mineral particles and this process has also been operative in the case of Ba to give relatively larger concentrations due to the larger ionic size of the latter. It is interesting to notice that the Sr $\times$ 10/Ca and Ba $\times$ 10/Ca ratios become high in horizons where Fe is beginning to increase also.

Lead substitutes for K quite readily and this may be the source in the parent material. Strong weathering is needed to alter the values appreciably and the silts show a tendency to accumulate Pb at the surface; a process which will be seen for clays also in Table 5. The similarity to K is more marked still in the case of Rb and the concentration at depth is even more marked than is that of K, due to the larger ionic size of the former.

In Table 5 are contained the values for minor elements for profiles 4 to 9 inclusive, and it can be seen that rather similar trends appear to those already discussed for profiles 1 and 3 in Table 4. Again Be, Mo, and Cs are below sensitivity, but here Sc is detected in all the clays and is higher in the podzols. Cr, V, Ni, Co, and Rb increase in concentration with depth and their concentration in the clay fraction is generally greater than in the silt fraction. Li, Sr, Ba, Sn, and Pb tend to be greater in quantity at depth in weakly leached profiles and the reverse in strongly leached ones, due, it seems, to organic matter. Zr and Y do not show this trend so well, and it indicates that some different process is at work. Silver, undetected in profiles 1 and 3, appears in these samples, especially the podzols.

Effects due to climatic variation are more difficult to evaluate, but a comparison of Tables 4 and 5 demonstrates that there are undoubted changes. These minor-element variations with climatic changes have two different causes; (1) organic matter, (2) mineralogical composition.

With an increase in rainfall and drop in annual mean temperature, more undecomposed humic material accumulates, a feature indicated previously when

mechanical analyses were considered, and moreover an observable fact in the field. The effects of this organic matter become strongly felt, due to the concentration of elements by vegetational metabolism. Under this heading comes the concentration of Sc and, even more, of Sn and Pb, in podzols formed under cool conditions. Under very cold conditions the formation of humus is impeded, and it seems that the forest litter does not contain a concentration of these elements so great as that of humus.

Mineralogical variation may be considered under three sub-factors: (a) camouflage or capture of elements within the clay mineral lattice, (b) adsorption of large ions on the edges of fine particles, (c) precipitation at the edges of particles. It has been demonstrated previously that the mineralogical assemblage due to weathering is feldspar → sericite → illite → kaolinite, the change from left to right being favoured by increase in temperature. The kaolinite lattice with both cations of relatively small size will not favour any substitution by large ions, and hence, with the exception of $Ga^{3+}$, possible exception of $Cr^{3+}$ and even less likely $Ni^{2+}$, the minor elements estimated would be excluded from the actual lattice (even Ga is lost relative to Al), and any concentrating factor would be due to adsorption of large ions on the lattice. This latter process must also of necessity be restricted, due to the low base-exchange properties of kaolinite. Precipitation of gels at clay edges could take place and is no doubt represented by $Fe^{3+}$ precipitation as $Fe_2O_3$. The occurrence of certain elements in the profiles would be favoured by lower temperatures, provided of course weathering reactions are not brought to a standstill; for under such conditions illite, or slightly hydrated mica, would allow greater freedom, since the presence of $Fe^{3+}$, $Fe^{2+}$, $Mg^{2+}$, and $K^+$ would permit considerable substitution within the lattice. Furthermore, as the exchange capacity of illite is greater than that for kaolinite, adsorption might also be expected to be stronger. Tests reveal a much greater concentration of $Rb^+$ under the cooler conditions. This is presumably replacing $K^+$ within the lattice, for in any competition for adsorption, notwithstanding its large ionic size, the $Rb^+$ is liable to be excluded by $Fe^{3+}$, of which there would be considerable amounts available. A somewhat similar but less marked effect is seen in the element Ba, whereas in Sr of smaller ionic size there is little if any difference. Cr and V are also greater in amount under the cooler conditions, presumably substituting for $Fe^{3+}$ in the lattice.

There are two exceptions to what would seem a general trend of loss of minor constituents with increasing leaching due to rise in temperature; these exceptions are Zr and, to a lesser extent, Y. The reason is believed to be due to the greater quantity of material leached in profiles 1 and 3 compared with the remainder. It would seem that in these northernmost profiles the Zr is rendered soluble from the mineral zircon and precipitated about the clays. In profiles 4-9 the process is very weak and little solution of Zr is effected. Thus profiles 1-3 may lie midway between the podzolizing and lateritization processes, for it has been shown that Zr concentrates strongly during lateritization (Goldschmidt, 1954).

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# The occurrence of germanium in blende

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ABSTRACT
The spectrochemical analysis of germanium in blende specimens, predominantly from British localities, is described. The results confirm the conclusions of other workers that germanium is present in highest concentration in blende deposited at low temperatures. The incorporation of germanium in blende is discussed in the light of size and valency considerations and the structure of the germanium sulphides.

As part of a general study at the Inorganic Chemistry Laboratory, Oxford, on trace elements in sulphide minerals, data has been accumulated on the occurrence of germanium in blende. Since germanium has recently become of industrial importance, particularly in the manufacture of transistors, and as a fair quantity of the metal can be obtained as a by-product from zinc extraction plants,† the occurrence of germanium in blende may become of considerable economic as well as of geochemical interest.

The radii and ionization potentials of the $Ge^{4+}$ and $Si^{4+}$ ions are similar ($Ge^{4+}$, $r = 0{\cdot}48$ Å, $I = 45{\cdot}7$ V; $Si^{4+}$, $r = 0{\cdot}42$ Å, $I = 45{\cdot}1$ V), and germanium replaces silicon in silicate mineral lattices (Goldschmidt, 1931; Harris, 1954b). Quite unlike silicon, however, germanium has a considerable chalcophile tendency, and traces of the element are found in blende from many widespread localities. Only a few rare minerals, such as argyrodite and germanite, contain germanium as a major constituent. In our investigation, germanium has been determined in blende specimens primarily from known localities in the British Isles, since further samples could then be obtained if required.

Particular attention has been given to those localities where the germanium content is high.

## Spectrochemical Analysis of Germanium in Blende

### *Introduction*

Many procedures for the analysis of traces of germanium have been described. A review of analytical methods for germanium up to 1952 has been given by Krause and Johnson (1953), and details of spectrochemical methods used for the determination of the element in mineralogical materials prior to 1950 have been given by Ahrens (1950). Among more recent spectrochemical procedures which should be mentioned are the interrupted-arc methods of Saito (1951, 1952), and Gotô and Yokoyama (1954), and the enrichment method of Harris (1954a).

In our analyses of germanium in blende specimens, a spectrochemical procedure using the cathode-layer carbon arc has been used. Details are given below.

### *Preparation of the specimens for analysis*

Most of the specimens analyzed spectrochemically were of quite good quality, and separations employing heavy liquids or magnetic methods appeared to be unnecessary. The mineral samples

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† For a description of commercial methods for the production of germanium, see O'Connor (1952). See Powell (1954) for details of the British Association meeting on germanium and gallium and their applications.

were first wrapped in filter paper and broken up in a hard-steel ore crusher. From the resulting fragments, which were examined under high magnification, small homogeneous crystals were separated by hand-picking. These were ground to a fine powder in an agate mortar, with the usual precautions as to the avoidance of contamination.

*The spectrochemical method used*

It was decided to employ a method with the zinc of the blende as an internal standard and with the analysis pair Ge 2754·6 Å and Zn 2756·5 Å. The observations were made using a Bellingham and Stanley medium spectrograph, with quartz optics. The electrodes for holding the samples were made from pure graphite rods, pieces of which were shaped and drilled as described by Ströck (1936) (cavity—1 mm internal diameter, 6 mm depth). Each sample-bearing electrode was made the cathode, while each upper electrode, the anode, was made of similar rod, and pointed. The optical conditions were such that an intermediate image of the arc was produced on a diaphragm which passed only light from the cathode-layer region; this was focused at the collimator by means of a spherical lens near the slit.

A d.c. arc discharge (110 volts on open circuit), carrying a current of 6 amps, excited the powdered specimens, and exposures were of 20 sec in each case. Spectra were recorded on Ilford S.R. panchromatic plates, which were developed at 18°C according to directions from the manufacturers.

Standard samples containing 1, 0·1, 0·01, 0·001, and 0·0001 per cent Ge were made by thoroughly dry-mixing pure $GeO_2$ and ZnS which was shown to be spectrographically free from germanium.

Plate calibration was achieved by mounting a seven-step sector immediately in front of the slit and exposing to an iron arc; the transmission of each step of an iron line in the region of the analysis pair was then measured with a Hilger non-recording microphotometer to give the characteristic curve.

The intensities of the analysis line Ge 2754·6 Å and the internal standard line Zn 2756·5 Å were compared by measuring their transmissions with the microphotometer and employing the characteristic curve. No correction was made for background. The ratio of the intensities of the analysis pair for the standard samples was plotted against germanium percentage composition on log-log co-ordinates to give the working curve. The ratio of the intensities of the line pair in the blende samples being determined in the same manner, their percentage germanium content could be read directly from the working curve.

The precision of this procedure was *c.* 10 per cent, and the minimum sensitivity was $<0{\cdot}001$ per cent Ge.

## Analytical Results

Results of the analyses of the germanium-enriched blende samples investigated are shown in Table 1. The numbers of the specimens are those of the Oxford University mineral collection. In those cases where blendes from regions investigated by Stoiber (1940) and Warren and Thompson (1945) have been examined, our germanium determinations correlate well with their semi-quantitative results.

## Geochemistry of the Occurrence of Germanium in Blende

*The distribution of germanium in blende*

As mentioned above, traces of germanium occur in silicate minerals camouflaged by silicon. Just as gallium appears to desert aluminium in silicates and enter blende, so germanium differs from silicon in entering the sulphide mineral.

Previous investigations on the occurrence of germanium in blende samples from various widespread localities (e.g., Goldschmidt and Peters, 1933; Graton and Harcourt, 1935; Stoiber, 1940; Oftedal, 1940; Preuss, 1941; Gabrielson,

*Table* 1. *Germanium in blende specimens*

| *Sample No.* | *Mineral locality* | *per cent* Ge |
|---|---|---|
| 13363 | Minera, Wrexham | 0·026 |
| 15303 | Isle of Man | 0·025 |
| 19242 | Wanlockhead, Dumfriesshire | 0·027 |
| 11021 | Laxey, Isle of Man | 0·025 |
| AWGK | Tankerville, Minsterley, Shropshire | 0·026 |
| 9350 | Halkyn, Flintshire | 0·067 |
| 11018 | Holywell, Flintshire | 0·067 |
| 14403 | Derbyshire | 0·028 |
| 11026 | Alston, Cumberland | 0·056 |
| 10231 | Webb City, Missouri, U.S.A. | 0·028 |

1945; Warren and Thompson, 1945; Evrard, 1945) have shown that the amount of the element present depends primarily on the mineralogical region, and is usually considerable only in blendes of low temperature of formation. Our analyses confirm this; for example, amongst the blendes from British localities investigated, those of high germanium content are all of the low- or medium-temperature type. In samples from high-temperature localities in Cornwall and from Gwynfynydd mine, Dolgelly, no germanium could be detected by our method of analysis.

The fact that germanium preferentially enters blendes formed at low temperatures from aqueous solutions can probably be correlated with its ready ability to form sulphogermanate ions in alkaline solutions.

The order of the germanium content of blendes from different regions is given in Table 2. The amount of the element in blendes formed at low temperatures is often greater than 0·005 per cent, and may in exceptional cases be as large as 0·3 per cent. In high-temperature blendes usually about 0·0005 per cent and rarely as much as 0·005 per cent is found. Comparison of these values with the figure of 0·0007 per cent for the abundance of germanium in igneous rocks (Rankama and Sahama, 1950, p. 98) indicates the considerable enrichment of the element in low-temperature blendes.

*Nature of the occurrence of germanium in blende*

It has long been known that one of the most important factors governing the entry of trace elements into the crystal lattices of minerals is the relative size of the atoms or ions. If the atomic or ionic diameters of two elements differ by more than about 15 per cent, substitution of one for another in a mineral is usually very restricted. Ahrens (1953) has demonstrated that substitution of one ion for another in a mineral is also regulated by the relative properties of polarization, and has used the ionization potential as a measure of the polarizing power of cations. An appreciable difference in ionization potential between two cations of the same charge and similar size would be a deterrent to much mutual substitution. This "ionic approach" has been shown to be readily applicable to the associations of

*Table 2. Germanium content of blendes in various regions*

| *Region* | *Temperature type of deposit* | *Range of germanium concentration (per cent)* | *References* |
|---|---|---|---|
| Cumberland, England | low | 0·01–0·06 | Warren and Thompson (1945), Cox (1949) |
| Derbyshire, England | low | 0·01–0·03 | Warren and Thompson (1945), Cox (1949) |
| Northern Pennines, England | low | 0·0001–0·01 | Neal (1948) |
| Flintshire, North Wales | low | <0·01–0·07 | Cox (1949) |
| Central Kentucky, U.S.A. | low | <0·01–0·1 | Stoiber (1940) |
| Mississippi Valley, U.S.A. | low | <0·01–>0·1 | Stoiber (1940), Warren and Thompson (1945) |
| European Mississippi Valley type (Belgium, Poland, Germany) | low | <0·01–0·1 | Stoiber (1940), Warren and Thompson (1945) |
| Paleozoic and mezozoic sediment deposits, Sweden | low | up to 0·003 | Gabrielson (1945) |
| Western Canada | low, medium high | very rarely >0·01 | Warren and Thompson (1945) |
| Cornwall, England | high | rarely >0·001 | Warren and Thompson (1945), Morris (1952) |
| Dolgelly, North Wales | high | <0·001 | Cox (1949), Morris (1952) |
| New South Wales, Australia | high | <0·001 | Warren and Thompson (1945), Anderson(1953) |
| Caledonian range, Norway | high | not >0·0005 | Oftedal (1940) |

various elements in minerals of predominantly ionic character, but only applies in a restricted way to substitutions in sulphide minerals where the bonds may possess considerable covalent or metallic character (see Frueh, 1954). However, Ahrens's principle would readily account for the entry of divalent germanium into blende in place of zinc, since the radii and ionization potentials of the $Ge^{2+}$ ion ($r = 0{\cdot}69$ Å, $I = 15{\cdot}93$ V) and the $Zn^{2+}$ ion ($r = 0{\cdot}69$ Å, $I = 17{\cdot}95$ V) are similar.

One disadvantage of the ionic approach to mineral formation is that it fails to predict the spatial disposition of bonds in crystals which are structurally non-ionic, although Ahrens has demonstrated regularities between such structures and ionization potentials. In considering substitutions in crystals of considerable covalent character, the availability of bond orbitals suited to the stereochemical arrangement imposed by the host crystal is important, in addition to size considerations. In the formation of covalent bonded structures the germanium atom, having the ground-state electronic configuration $KLM4s^24p^2$, can be expected to form tetrahedral $sp^3$ bonds rather than octahedral bonds, which would involve the use of the $5d$ level. This is in agreement with the fact that germanium is found to occur predominantly in blende and other sulphidic minerals of tetrahedral rather than octahedral structure.

The crystal structures of both the germanium sulphides GeS and $GeS_2$ have been determined (Zachariasen, 1932 and 1936). The environment of the germanium atoms in these compounds and of the zinc atoms in blende is:

| GeS | $GeS_2$ | ZnS(blende) |
|---|---|---|
| Ge { 1S 2·47 Å; 2S 2·64; 1S 2·91; 2S 3·00 | Ge { 4 equidistant S atoms at 2·19 Å | Zn { 4 equidistant S atoms at 2·35 Å |

The monosulphide GeS possesses a distorted structure, while in the disulphide each germanium atom is surrounded tetrahedrally by four sulphur atoms. Although the Ge-S distance in the disulphide is shorter than the Zn-S distance in blende, the difference is well within the limits to permit the substitution of tetrahedrally bound germanium as proxy for zinc in the mineral. Despite the fact that the germanium atom has a greater number of electrons than the zinc atom, this inclusion of germanium in blende, in place of zinc, may be considered possible without postulating concomitant substitutions of atoms with a smaller number of valency electrons, since the additional electrons may enter the conduction band of the crystal, or positive holes may be produced.

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# Metamorphism of natural waters in the crust of weathering—2*

I. I. Chebotarev
Australia

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Part 2


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## Study of the Problem

### *Hydraulics and salinity of subterranean waters*

#### *Types of the artesian "systems"*

The rate of movement of natural waters in the subsurface reservoir and the variation in salinity are largely determined by the hydrogeological structure of the basin and its recharge-discharge conditions.

The following subdivision of the subsurface basins containing confined water, or the so-called artesian "systems", can be given in this respect:

1. *Open* basins.
2. *Partly closed* basins.
3. *Closed* basins.

* Part 1 of this article has been published in *Geochim. et Cosmochim. Acta* **8**, 22.

*Open* basins are found in the localities where the water-bearing formation containing artesian and subartesian waters in upper portion of the area is drained by the rivers or lakes in lower area (Antelopa Valley, California, the Ukrainian basin, and others).

*Partly closed* basins are found in the areas in which the pressure (artesian and subartesian) waters are drained by bores only in one portion of the basin: whereas in the other portion, located in the vicinity, pressure waters are discharged by springs (the Great Australian Basin, for instance, where the "mount springs" are numerous).

*Closed* basins, in which the outlet of the porous water-bearing bed at the lower level is presumably found on the floor of the sea.

It is believed that in the closed basins a certain but unknown amount of pressure-water may be spent on the general leakage through the impermeable strata, all of which permit the escape of an appreciable portion of pressure-water (South Dakota, Pre-Caucasian Basins, Turkestan).

The intensity of water-exchange between surface and subterranean waters is largely dependent upon the rate of flow in the intake area and by the drainage conditions in the area of discharge. The later one is usually directed seawards or, after all, towards the oceanic depressions.

In some large structural units a local drainage of deep-seated water may be caused by the occurrence of the tectonic breakings, but the rate of such drainage would not be significant.

In most artesian "systems" of the closed type, water-exchange is more intensive on the slopes of the structure, while in the inner portions very often sluggish movement occurs.

As a result of this process, a great variation in chemical composition of subterranean waters takes place; bicarbonate waters prevail on the slopes of the structure, while sulphate and chloride waters occur in the deeper portions of the basin.

*Hydraulic gradients and salinity*

It is one of the theses of the present study that the variation in salinity of natural waters in the crust of weathering is a function of the hydrodynamics of the underground flow and that it is determined first of all by the rate of the hydraulic gradients (Tables 14, 15, 16, 17).

*Depth and salinity of water*

The relation between the depth of the occurrence and salinity of subterranean waters in the crust of weathering is twofold.

As a general law the geochemical types of natural waters depend on the water-exchange possibility: bicarbonate waters occur near the earth's surface and chloride waters in the deeper portions of the structures (Tables 18, 19).

A deviation of this law often occurs when the local structural conditions of the water-bearing bed facilitate the active water-exchange in the subsurface reservoir (Tables 20 and 21).

The depth of the active exchange is variable, but sometimes it is considerable

| Group of bores | Static water level, feet above S.L. | Hydraulic gradient | | Total salinity | | Mode of reporting | Cations | | | Anions | | | Class of water |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Observed | % | p.p.m. | % | | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3 + CO_3$ | |
| First | 340 | 0·013 | 100·0 | 1,307 | 100·0 | p.p.m. | 257 | 101 | 86 | 453 | 251 | 159 | |
| | | | | | | React. value % | 24·0 | 10·8 | 15·2 | 27·4 | 11·2 | 11·4 | IV |
| | 240 | 0·003 | 23·0 | 2,046 | 156·0 | p.p.m. | 442 | 137 | 124 | 974 | 281 | 88 | |
| | | | | | | React. value % | 26·5 | 9·4 | 14·1 | 37·8 | 8·0 | 4·2 | V |
| Second | 350 | 0·01 | 100·0 | 1,663 | 100·0 | p.p.m. | 367 | 112 | 91 | 587 | 349 | 157 | |
| | | | | | | React. value % | 26·2 | 9·6 | 14·2 | 28·5 | 12·5 | 9·0 | IV |
| | 270 | 0·0076 | 76·0 | 2,337 | 140·0 | p.p.m. | 473 | 174 | 152 | 1,166 | 281 | 91 | |
| | | | | | | React. value % | 24·6 | 10·3 | 15·1 | 39·4 | 6·8 | 3·8 | V |
| | 233 | 0·0014 | 14·0 | 3,215 | 192·0 | p.p.m. | 570 | 256 | 244 | 1,527 | 483 | 135 | |
| | | | | | | React. value % | 21·5 | 17·4 | 11·1 | 36·5 | 8·7 | 4·8 | V |
| Third | 384 | 0·03 | 100·0 | 528 | 100·0 | p.p.m. | 140 | 30 | 26 | 170 | 35 | 127 | |
| | | | | | | React. value % | 31·3 | 7·7 | 11·0 | 24·6 | 3·7 | 21·7 | III |
| | 300 | 0·0045 | 15·0 | 890 | 170·0 | p.p.m. | 234 | 43 | 43 | 323 | 118 | 129 | |
| | | | | | | React. value % | 32·1 | 6·7 | 11·2 | 28·1 | 7·7 | 14·2 | IV |
| | 142 | 0·0019 | 6·3 | 2,628 | 498·0 | p.p.m. | 668 | 116 | 128 | 1,076 | 505 | 135 | |
| | | | | | | React. value % | 32·0 | 6·4 | 11·6 | 33·4 | 11·6 | 5·0 | V |
| Fourth | 423 | 0·0037 | 100·0 | 7,433 | 100·0 | p.p.m. | 1,805 | 341 | 375 | 3,044 | 1,737 | 131 | |
| | | | | | | React. value % | 31·0 | 6·7 | 12·3 | 34·0 | 14·3 | 1·7 | V |
| | 373 | 0·0029 | 78·4 | 8,170 | 109·0 | — | — | — | — | — | — | — | |
| | 280 | 0·0019 | 51·3 | 9,743 | 131·0 | p.p.m. | 2,420 | 341 | 473 | 3,213 | 3,146 | 150 | |
| | | | | | | React. value % | 32·6 | 5·3 | 12·1 | 28·1 | 20·4 | 1·5 | V |

*Table* 15. *Relationship between hydraulic gradients and salinity of subterranean waters in South Dakota Artesian Basin (Dakota sandstone)* (Darton, 1909)*

| *Locality of wells* | *Static level, feet above sea level* | *Hydraulic gradient* | | *Total salinity* | | *Mode of reporting* | *Cations* | | | *Anions* | | | *Class of water* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *Observed* | % | *p.p.m.* | % | | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3 + CO_3$ | |
| Butte County Well 1½ miles below Belle Fourche | 3,100 | 0·003 | 100·0 | 560·8 | 100·0 | p.p.m. | 153·7 | 9·7 | 2·4 | 16·2 | 140·9 | 237·9 | |
| | | | | | | React. value % | 45·3 | 3·3 | 1·4 | 3·2 | 20·2 | 26·6 | III |
| Stanley County Wendte Station | 2,100 | 0·0008 | 26·6 | 3,487·1 | 622·0 | p.p.m. | 1,401·7 | 11·5 | 5·5 | 1,380 | — | 688·4 | |
| | | | | | | React. value % | 49·2 | 0·5 | 0·3 | 28·3 | — | 21·7 | III |

* *Remarks:* All computations including the reconversion of the water analyses from hypothetical compounds into the ionic form have been done by the present writer.

*Table* 16. *Relation between hydraulic gradients and salinity of subterranean waters in the San Diego area, California*
(Ellis *and* Lee, 1919)

| *Locality of wells* | *Static level feet above S.L.* | *Haydraulic gradient* | | *Total salinity* | | *Mode of reporting* | *Cations* | | | *Anions* | | | *Class of water* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *Observed* | % | *p.p.m.* | % | | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3$ + $3O_3$ | |
| Sect. 23 Quarter E½; Well 042 | 41 | 0·006 | 100·0 | 642 | 100·0 | p.p.m.<br>React. value % | 115<br>26·3 | 51<br>10·1 | 24<br>13·3 | 166<br>24·5 | 30<br>4·0 | 256<br>21·5 | III |
| Sect. 23 Quarter NW; Well 040 | 18·1 | 0·0043 | 71·0 | 1,304 | 203·0 | p.p.m.<br>React. value % | 309<br>30·1 | 94<br>10·6 | 50<br>9·3 | 630<br>41·0 | 84<br>3·9 | 137<br>5·1 | IV |
| Sect. 23 Quarter NW; Well 034 | 3·5 | 0·0027 | 45·0 | 3,277 | 510·0 | p.p.m.<br>React. value % | 733<br>29·7 | 244<br>11·4 | 116<br>8·9 | 1,214<br>32·2 | 658<br>3·0 | 312<br>4·8 | V |

* *Remarks:* All computations have been done by the present writer.

*Table* 17. *Relation between hydraulic gradients and salinity of subterranean waters in Comal County, Texas* (Hastings *et al.*, 1952)*

| *Locality of wells* | *Static level, feet above S.L.* | *Hydraulic gradient* | | *Total salinity* | | *Mode of reporting* | *Cations* | | | *Anions* | | | *Class of water* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *Observed* | % | *p.p.m.* | % | | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3 + CO_3$ | |
| Eugene Krause F70 | 650 | 0·008 | 100·0 | 168 | 100·0 | p.p.m. | 5 | 34 | 4 | 15 | 31 | 79 | |
| | | | | | | React. value % | 5·0 | 37·7 | 7·3 | 9·0 | 13·5 | 27·5 | III |
| Persy Hausman H28 | 640 | 0·0005 | 6·3 | 840 | 500·0 | p.p.m. | 85 | 72 | 57 | 124 | 63 | 439 | |
| | | | | | | React. value % | 15·3 | 15·3 | 19·4 | 14·6 | 5·4 | 30·0 | III |
| E. A. Burket H2 | 630 | 0·0003 | 3·7 | 2,134 | 1,270·0 | p.p.m. | 380 | 166 | 110 | 630 | 500 | 348 | |
| | | | | | | React. value % | 24·4 | 12·3 | 13·3 | 26·2 | 15·3 | 8·5 | IV |

* *Remarks:* All computations have been done by the present writer.

*Table* 18. *Change in salinity and types of subterranean waters with depth in paleozoic formations of the Kama River area (Europe)* (USUPOV, 1948)

| *Strata* | *Altitude of static level (feet)* | *Total salinity* | | *Reacting value in percent* | | | | | | *Class of water* |
|---|---|---|---|---|---|---|---|---|---|---|
| | | *p.p.m.* | *Relative salinity* | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3$ | |
| Upper Permian | +197 | 332 | 1·0 | 3·2 | 37·1 | 9·7 | 1·4 | 3·2 | 45·4 | I |
| Lower Permian | +74 | 482·4 | 1·45 | 9·5 | 18·2 | 22·3 | 2·1 | 11·9 | 36·0 | II |
| Lower Permian | +61 | 3,367 | 10·1 | 30·5 | 9·8 | 9·7 | 22·3 | 10·5 | 7·2 | IV |
| Lower Permian | −69 | 5,279 | 15·9 | 31·0 | 10·1 | 8·9 | 23·6 | 23·7 | 2·7 | V |
| Upper Carboniferous | −534 | 12,926 | 38·3 | 34·6 | 8·4 | 7·0 | 33·8 | 15·4 | 0·8 | V |
| Middle Carboniferous | −2,023 | 118,291 | 356·3 | 38·3 | 6·4 | 5·3 | 48·6 | 1·2 | 0·2 | V |
| Lower Carboniferous | −3,369 | 336,020 | 1,012·1 | 38·2 | 8·6 | 3·2 | 49·7 | 0·2 | 0·1 | V |

*Table* 19. *Variation in salinity of subterranean waters with depth in crystalline and metamorphic rocks of the north-western part of Central Asia* (MARINOV, 1948)

| *Type of rock* | *Depth (feet)* | *Total salinity* | | *Reacting value in percent* | | | | | | *Class of water* |
|---|---|---|---|---|---|---|---|---|---|---|
| | | *p.p.m.* | *percent* | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3$ | |
| Porphyrite | 56 | 506 | 100·0 | 20·6 | 9·0 | 20·4 | 4·0 | 9·7 | 36·3 | II |
| | 121 | 692 | 136·0 | 29·0 | 21·0 | — | 4·5 | 12·1 | 33·4 | II |
| | 154 | 1,642 | 324·0 | 25·2 | 24·8 | — | 12·7 | 21·8 | 15·5 | III |
| Schist | 68 | 608 | 100·0 | 22·6 | 27·4 | — | 5·7 | 8·1 | 36·2 | II |
| | 92 | 1,530 | 251·0 | 23·9 | 26·1 | — | 12·0 | 24·9 | 13·1 | IV |
| | 259 | 6,631 | 1,090·0 | 25·2 | 24·8 | — | 35·3 | 12·5 | 2·2 | V |

*Table* 20. *Change in salinity of subterranean waters with depth in Recent-Tertiary bed* (WARD, 1946)*

| *Depth (feet)* | *Salinity* | | *Strata* | *Supply* | *Depth (feet)* | *Salinity* | | *Strata* | *Supply* |
|---|---|---|---|---|---|---|---|---|---|
| | *p.p.m.* | *percent* | | | | *p.p.m.* | *percent* | | |
| 10 | 61,061 | 100·0 | Recent | None | 210 | 12,956 | 21·0 | Tertiary | Small |
| 80 | 78,764 | 129·0 | Pleistocene | None | 240 | 11,040 | 18·0 | Tertiary | Small |
| 150 | 45,174 | 74·0 | Pleistocene | None | 241 | 917 | 1·5 | Tertiary | Flowing |
| 190 | 28,271 | 46·0 | Pleistocene | None | 266 | 966 | 1·6 | Tertiary | Flowing |

* *Remarks:* Own computation.

(5,000–7,000 feet). The Great Australian Artesian Basin is one of the remarkable instances of such conditions (see further).

In New Zealand the water from 2,050 feet to 2,150 feet is as saline as sea-water, and at 3,000 feet and deeper some wells yield water with twice that salinity concentration (Henderson, 1943).

*Table* 21. *Change in salinity and types of subterranean waters with depth in South Carolina* (Stephenson, 1914)*

| *Depth* (*feet*) | *Total salinity* | | *Reacting value in percent* | | | | | | *Class of water* |
|---|---|---|---|---|---|---|---|---|---|
| | *p.p.m.* | *percent* | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3 + CO_3$ | |
| 425 | 3,449 | 100·0 | 46·9 | 0·8 | 2·3 | 36·4 | 4·8 | 8·8 | IV |
| 1,260 | 2,655 | 77·0 | 48·5 | 0·8 | 0·7 | 27·1 | — | 22·9 | III |
| 2,007 | 1,051 | 30·0 | 49·5 | 0·4 | 0·1 | 6·7 | 0·5 | 42·8 | I |

* *Remarks:* Own computation.

*Salinity variation with distance from the outcrop*

The change in salinity of subterranean waters in the same water-bearing zone but at different distances from the outcrop of the formation is characterized by the data in Tables 22 and 23.

In the Arbuckle Mountain area (Oklahoma) the salinity concentration in subterranean water increases from 10,000 p.p.m. to 150,000 p.p.m. in the distance of 14 miles, or at the rate of 10,000 p.p.m. per mile. In the area laying westward

*Table* 22. *Salinity variation of subterranean waters with distance from the outcrop*

A. *Midway Oil Field, California* (Rogers, 1917)

| *Distance from outcrop* (*feet*) | *Total salinity* (*p.p.m.*) | *Classes of water** | *Remarks* |
|---|---|---|---|
| 9,000 | 12,581 | III | * Own computation |
| 15,000 | 24,090 | IV | |
| 21,500 | 32,193 | V | |
| 27,300 | 34,889 | V | |

B. *Dakota Basin* (McCoy *and* Keyte, 1934)

| *Distance from outcrop* (*miles*) | *Depth* (*feet*) | *Total salinity* (*p.p.m.*) |
|---|---|---|
| 20 | 100–400 | 300–2,400 |
| 35 | — | 5,000 |

from the Ozarks the concentration increases at the rate of 1,200 p.p.m. per mile in a distance of 125 miles, and in Minnesota and Wisconsin (southward from the Canadian shield) 315 p.p.m. per mile is a distance of 225 miles (Dott and Ginter, 1930).

The increase in salinity concentration in water with the westward distance from the outcrop area and with increased depth and with the area of high depth of the water-bearing rock below the surface is also well known in Southern Kansas (Abernathy, 1948) and in West Texas Permian Basin (Berger and Fash, 1934). A similar phenomenon has been recorded in Europe (Ignatovich, 1944).

*Table 23. Salinity variation of subterranean water in the Permian rock of the Kama River region (Europe) along the line of dip of the rocks* (Kuznetzov, 1943)

| *Locality* | *Depth (feet)* | *Density 20°C* | *Parts per million* | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | *Total salinity* | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3$ |
| Levahino well 4 | 130–617 | 1·032 | 42,255 | 13,648 | 1,219 | 721 | 21,569 | 4,842 | 256 |
| Ust-Kachka well 19 | 388–969 | 1·077 | 105,239 | 37,209 | 2,162 | 866 | 59,989 | 4,831 | 182 |
| Nytva well 21 | 749–777 | 1·163 | 206,767 | 64,716 | 10,313 | 3,399 | 126,851 | 945 | 543 |

*Salinity variation with distance from the sea*

The increase in the amount of dissolved solids in the underground water in the alluvium towards the sea is illustrated by the data in Table 24.

Normally the salinity concentration in underground water towards the sea is due to its enrichment by soluble matter in the zone of chloride-sulphate accumulation (Fig. 2).

Sea-water contamination, as it has been observed in the Miami area, Florida, for instance, takes place only within a narrow coastal strip about one to two miles of the coast line (Brown, 1925; Love, 1945).

The occurrence of salt water due to sea-water intrusion has been recorded in twenty underground water-basins along the Californian Coast and inland bays where the water-bearing formations are apparently open to sea-water and the seaward hydraulic gradient has been reversed as a result of the protracted pumping draft (Banks and Richter, 1953).

*Table 24. Change in salinity of underground water in the alluvium of the Azapa Valley towards the sea* (Taylor, 1949)

| *Distance inland from the shore (km)* | Cl *(p.p.m.)* | *Total hardness as* $CaCO_3$ | *Distance inland from the shore (km)* | Cl *(p.p.m.)* | *Total hardness as* $CaCO_3$ |
|---|---|---|---|---|---|
| 17·7 | 100 | 260 | 5·0 | 160 | 320 |
| 15·7 | 120 | 270 | 1·4 | 170 | 360 |
| 8·4 | 130 | 320 | 1·1 | 190 | 350 |
| 6·6 | 150 | 310 | 0·05 | 210 | 380 |

*Depth and salinity of water in the Great Artesian Basin*

The data in Tables 25–30 and in Figs. 11–14 give an indication of the range of depth and salinity-variation of shallow and pressure-waters in the Great Australian Artesian Basin* (Fig. 10).

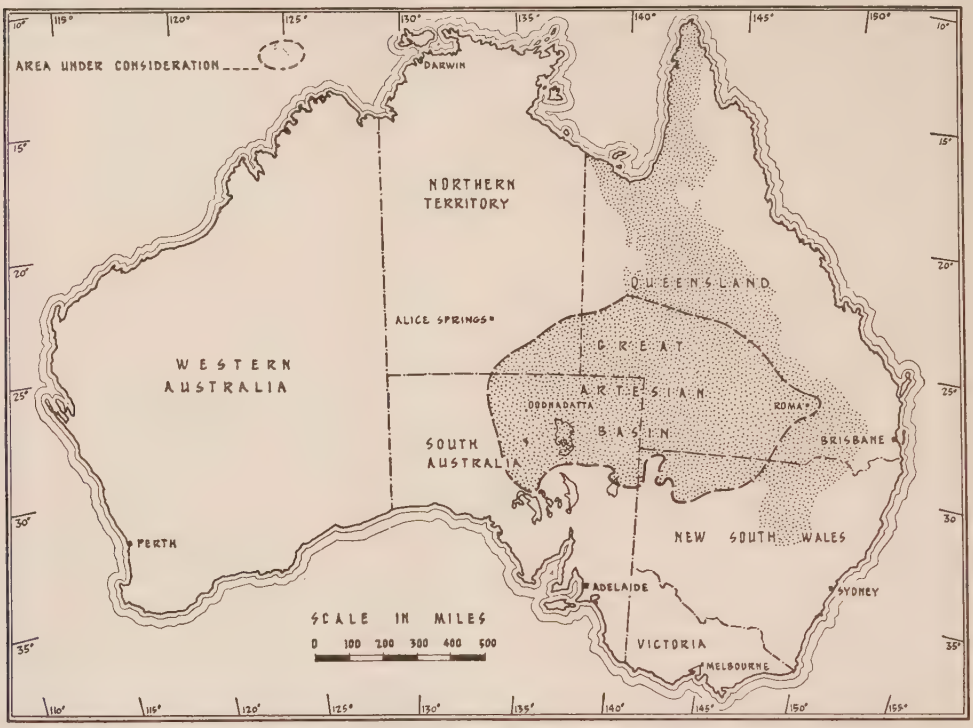


Fig. 10. Locality plan for the Great Artesian Basin.

A *Table 25. Depth to water in the Great Artesian Basin (chiefly bicarbonate waters)*

| *Rating of depth (feet)* | *South Australia* | | *Queensland* | | *New South Wales* | |
|---|---|---|---|---|---|---|
| | *Frequency* | | | | | |
| | *Number of bores* | *percent* | *Number of bores* | *percent* | *Number of bores* | *percent* |
| 0–1,000 | 818 | 89·0 | 1,105 | 65·9 | 8 | 8·1 |
| 1,000–2,000 | 83 | 9·1 | 356 | 21·2 | 40 | 40·4 |
| 2,000–3,000 | 6 | 0·6 | 139 | 8·3 | 39 | 39·4 |
| 3,000–4,000 | 10 | 1·0 | 66 | 3·9 | 12 | 12·1 |
| 4,000–5,000 | 2 | 0·2 | 12 | 0·7 | — | — |
| 5,000–6,000 | 1 | 0·1 | — | — | — | — |
| Total | 920 | 100·0 | 1,678 | 100·0 | 99 | 100·0 |

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*Table 25 (continued)*

B

| *Portion of the basin* | *Number of bores studied* | *Percentage of bore* | | | | |
|---|---|---|---|---|---|---|
| | | 1·0 | 25·0 | 50·0 | 75·0 | 99·0 |
| | | *Depth in feet* | | | | |
| South Australia | 920 | 2,481 | 577 | 177 | 49 | — |
| Queensland | 1,678 | 4,664 | 1,297 | 589 | 221 | 92 |
| New South Wales | 99 | 4,277 | 2,455 | 1,881 | 1,406 | 614 |
| TOTAL | 2,697 | — | — | — | — | — |

*Remarks:* Total amount of boreholes accounted in the Great Artesian Basin is now about 5,000. The deepest bore as yet known is in excess of 7,000 feet, being somewhere near the north-east corner of South Australia.

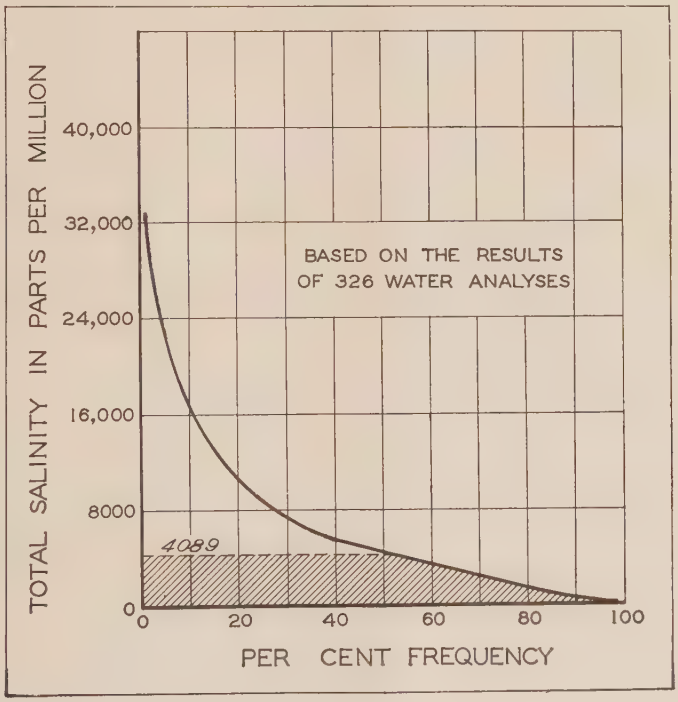


Fig. 11. Integral frequency curve of total salinity in shallow underground water in the Great Artesian Basin.

*Table 26. Total salinity of shallow underground waters in the South Australian portion*

| *Rating of total salinity (p.p.m.)* | *Frequency* | |
|---|---|---|
| | *Number of analyses* | *percent* |
| 0–5,720 | 217 | 66·6 |
| 5,720–11,440 | 75 | 23·1 |
| 11,440–17,160 | 25 | 7·6 |
| 17,160–22,880 | 3 | 1·0 |
| 22,880–28,600 | 1 | 0·3 |
| 28,600–34,320 | 2 | 0·5 |
| 34,320–40,040 | 1 | 0·3 |
| 40,040–45,760 | 1 | 0·3 |
| 45,760–51,480 | 0 | 0 |
| 51,480–57,200 | 1 | 0·3 |
| Total | 326 | 100·0 |

*Table 27. Total salinity of pressure waters (Cretaceous and Jurassic) in the Great Artesian Basin*

A

| *Rating of total salinity (p.p.m.)* | *South Australia* | | *Queensland* | | *New South Wales* | |
|---|---|---|---|---|---|---|
| | *Frequency* | | | | | |
| | *Number of analyses* | *percent* | *Number of analyses* | *percent* | *Number of analyses* | *percent* |
| 0–5,720 | 325 | 59·7 | 333 | 93·3 | 504 | 98·6 |
| 5,720–11,440 | 132 | 24·3 | 11 | 3·0 | 3 | 0·6 |
| 11,440–17,160 | 59 | 10·9 | 6 | 1·7 | 0 | 0 |
| 17,160–22,880 | 12 | 2·2 | 5 | 1·4 | 1 | 0·2 |
| 22,880–28,600 | 7 | 1·3 | 1 | 0·3 | 3 | 0·6 |
| 28,600–34,320 | 2 | 0·3 | 0 | 0 | 0 | 0 |
| More than 34,320 | 7 | 1·3 | 1 | 0 | 0 | 0 |
| Total | 544 | 100·0 | 357 | 100·0 | 511 | 100·0 |

B

| *Portion of the basin* | *Number of analyses* | *Percentage of analyses* | | | | | *Relative salinity* |
|---|---|---|---|---|---|---|---|
| | | 1·0 | 25·0 | 50·0 | 75·0 | 99·0 | |
| South Australia | 544 | 42,413 | 9,853 | 3,732 | 1,201 | — | 852·0 |
| Queensland | 357 | 17,088 | 3,330 | 972 | 243 | — | 222·0 |
| New South Wales | 511 | 7,636 | 1,487 | 438 | 109 | — | 100·0 |
| Total | 1,412 | — | — | — | — | — | |

*Table 28. Total salinity of the Jurassic waters in South Australian portion of the Great Artesian Basin*

A

| *Frequency* | *Rating of total salinity (p.p.m.)* | | | | *Total* |
|---|---|---|---|---|---|
| | 0–1,716 | 1,716–3,432 | 3,432–5,148 | *More than* 5,148 | |
| Number of analyses | 44 | 46 | 19 | 9 | 118 |
| Percent | 37·3 | 39·0 | 16·1 | 7·6 | 100·0 |

B

| *Number of water analyses* | *Percentage of analyses* | | | | |
|---|---|---|---|---|---|
| | 1·0 | 25·0 | 50·0 | 75·0 | 99·0 |
| | *Total salinity (p.p.m.)* | | | | |
| 118 | 7,058 | 3,217 | 2,273 | 1,367 | 137 |

*Table 29. Hydrochemical facies of subterranean waters of the Great Artesian Basin*

| *Types of waters* | *Total salinity (p.p.m.)* | | | *No. of analyses* |
|---|---|---|---|---|
| | *Low saline facies* | *Transitional facies* | *High saline facies* | |
| Shallow water | Less than 1,687 | 4,089 | More than 8,223 | 326 |
| Pressure-water (no subdivided) | | | | |
| (1) South Australia | Less than 1,201 | 3,732 | More than 9,853 | 544 |
| (2) Queensland | Less than 243 | 972 | More than 3,330 | 357 |
| (3) New South Wales | Less than 109 | 438 | More than 1,487 | 511 |
| Jurassic pressure-waters (S.A. portion) | Less than 1,367 | 2,273 | More than 3,217 | 118 |
| Total analyses | | | | 1,856 |

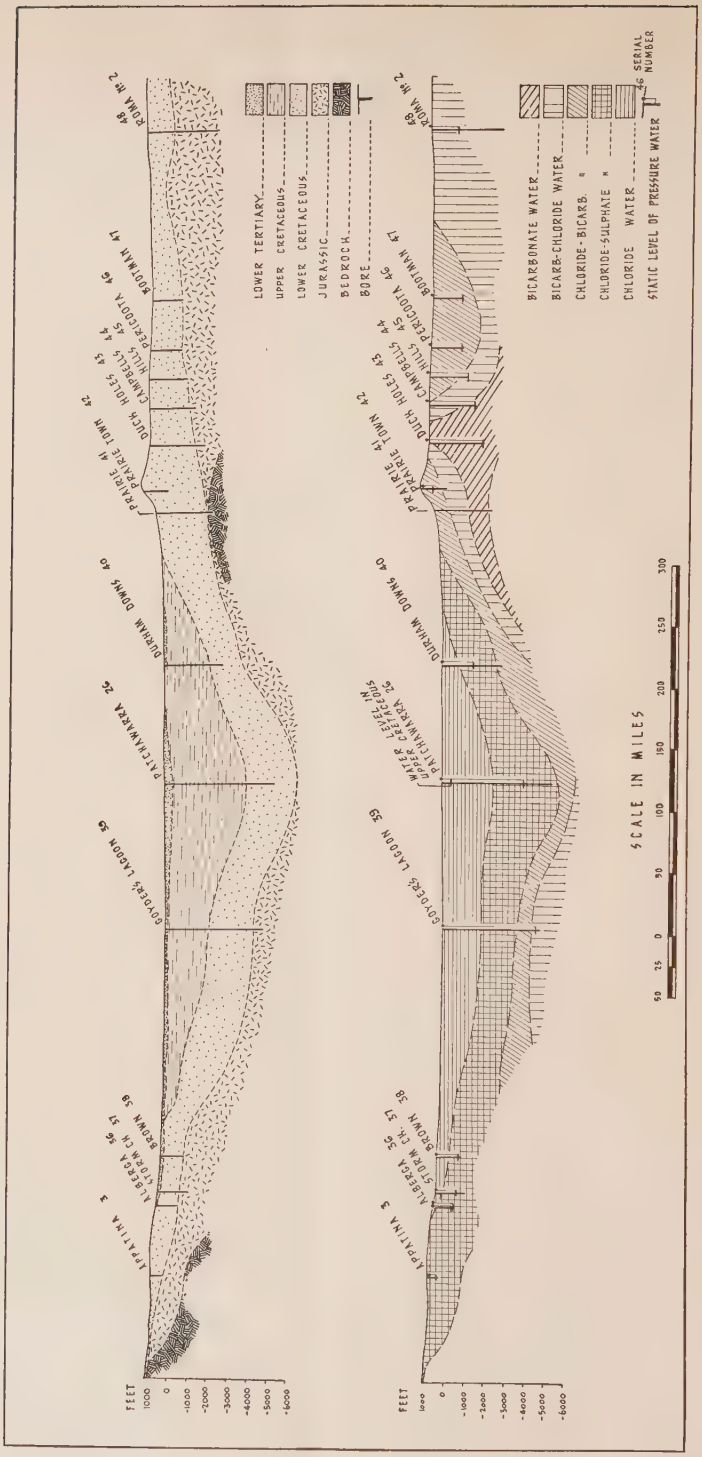


Fig. 12. Geological and geochemical transverse section of the Great Artesian Basin.

*Table* 30. *Composition of representative subterranean waters of different geochemical types in the Great Artesian Basin*

| *Portion of basin and bore location* | *Water-bearing bed* | *Total salinity (p.p.m.)* | *Reacting value in percent* | | | | | | *Class of water* |
|---|---|---|---|---|---|---|---|---|---|
| | | | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3$ | |
| *South Australia* | | | | | | | | | |
| Nick O'Time | L. Cretaceous | 31,992 | 32·6 | 13·1 | 4·3 | 46·9 | 3·1 | — | V |
| Meteor | L. Cretaceous | 1,233 | 49·8 | — | 0·2 | 12·4 | 0·1 | 37·5 | II |
| Patchawarra | L. Cretaceous | 2,807 | 49·2 | 0·4 | 0·4 | 35·6 | 0·4 | 14·0 | IV |
| Oodnadatta | Jurassic | 2,167 | 35·4 | 2·6 | 12·0 | 33·0 | 10·0 | 7·0 | IV |
| Peachawirrina | Jurassic | 1,571 | 47·5 | 1·8 | 0·7 | 24·0 | 0·1 | 25·9 | III |
| Sinclair | Jurassic | 1,030 | 48·2 | 0·3 | 1·5 | 11·9 | — | 38·1 | II |
| *Queensland* | | | | | | | | | |
| Tambo | Jurassic | 143 | 37·4 | 5·2 | 7·4 | 16·2 | — | 33·8 | II |
| Cunnamula | Jurassic | 368 | 50·0 | — | — | 2·0 | — | 48·0 | I |
| Eromanga | Jurassic | 1,997 | 49·4 | 0·6 | — | 4·3 | 1·0 | 44·7 | I |
| Winton | Jurassic | 373 | 41·0 | 9·0 | — | 13·0 | — | 37·0 | II |
| Longreach | Jurassic | 782 | — | — | — | 17·8 | — | 32·2 | II |
| *New South Wales* | | | | | | | | | |
| Coonamble | — | 729 | 48·8 | 0·8 | 0·4 | 5·5 | — | 44·5 | I |
| Narba | — | 736 | 45·7 | 1·8 | 2·5 | 4·4 | 0·5 | 45·1 | I |

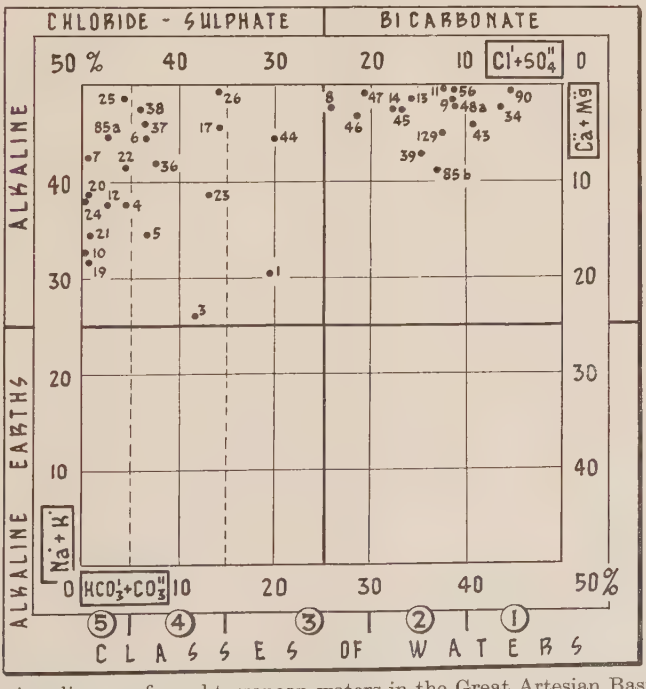


Fig. 13. Classification diagram for subterranean waters in the Great Artesian Basin. Some figures refer to bore numbers on Fig. 12; ions in reacting value in percent. Tertiary waters: 19, 20, 21; Cretaceous waters: 7, 10, 11, 12, 13, 24, 85a; Jurassic waters: 1, 3, 4, 5, 6, 8, 9, 14, 17, 22, 23, 25, 26, 34, 36, 37, 43, 44, 45, 46, 47, 48a, 56, 85, 90, 129.

## *Subterranean waters in oilfield*

### *Substance of the problem*

The great importance of subterranean waters in the migration, accumulation, preservation, and destruction of the oil and gas occurrences as well as one of the forces for the production of oil has been well recognized all over the world.

Water is found in nearly all oilfields, but unfortunately not only the geochemical relationship of water to oil and gas remains largely unknown, but even the problem related to the chemical character of the waters themselves, their salinity concentration, the ionic content, the occurrence and role of sulphate, and the concentration of carbonate in the petroliferous zones, etc., have not yet been systematically studied.

For this reason, the scientific interpretation of the factual data and the identification and correlation of the oilfield waters of the different chemical composition as a criterion in search for oil have been hindered.

As the accumulation and the analysis of the data related to the chemical composition of the oilfield waters has proceeded in the course of the present study, it has become apparent that many of the old concepts about the chemical nature of the waters have been completely disproved and the new aspect of the problem has been indicated.

We definitely know now that the subterranean waters associated with oil-pools are not necessary to be chloride brines or the water of extremely low sulphate content is typical for the oilfields.

It is also now evident that the variety in chemical composition of oilfield waters is mainly determined by the various types of the traps of petroleum (stratigraphic, structural) as well as by the dynamics of water itself.

Thus in the stratigraphic complexes which are found in the zone of the intensive flush the chemical composition of water will be completely different from that found in the zone of the limited circulation and hampered drainage.

The highly concentrated chloride water is mainly associated with those oil-pools where the conditions for the preservation of the original oil occurrences were favourable (stagnant conditions).

But even in this area the subterranean waters of high salinity have been eventually segregated during the prolonged period of the inter-reservoir migration metamorphisation and preservation.

Many hundreds of water analyses from the different oil-pools in the world have been classified and considered in this chapter, and it is believed that this information would be of some interest and practical value for students in the field of petroleum.

### *Method of grouping*

The assorted data related to the depth of occurrence and salinity variation of subterranean waters in the oilfield areas in the world (Table 31) have been collected chiefly from published sources (3, 10, 14, 17, 18, 19, 20, 22, 26, 27, 28, 29, 32, 34, 35, 39, 42, 45, 47, 48, 49, 52, 53, 54, 57, 62, 63, 66, 67) and are grouped according to the geochemical types of waters. The analysis of these data has been carried out by means of the aforementioned principles of the theory of frequency.

*Table 31. Summary data related to the oilfield waters in the world*

| *Major groups of water* | *Number of bores with depth to water* | *Number of analyses* | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | *Total salinity* | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3$ |
| Bicarbonate waters | 34 | 630 | 618 | 630 | 629 | 629 | 629 | 630 |
| Sulphate waters | 28 | 256 | 256 | 256 | 256 | 256 | 256 | 256 |
| Chloride waters | 605 | 967 | 939 | 933 | 939 | 943 | 940 | 936 |
| TOTAL | 667 | 1,853 | 1,813 | 1,819 | 1,824 | 1,828 | 1,825 | 1,822 |

*Depth of water*—The depth of the occurrence of subterranean waters of the different geochemical types in the oilfield areas is shown in Table 32 and Fig. 14.

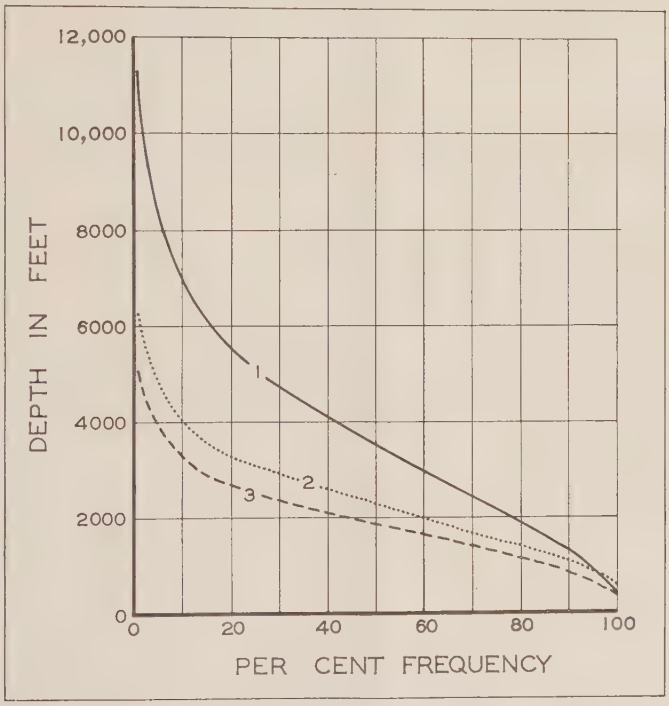


Fig. 14. Integral frequency curves of depth of chloride (1), bicarbonate (2), sulphate (3) waters in the oilfield areas.

*Chemical composition of water*

*Bicarbonate waters*—The salinity distribution of bicarbonate waters is shown in Table 33 and Fig. 15.

The data presented in Table 34 show a modification of bicarbonate waters of low saline facies associated with oil in a relatively short period of time.

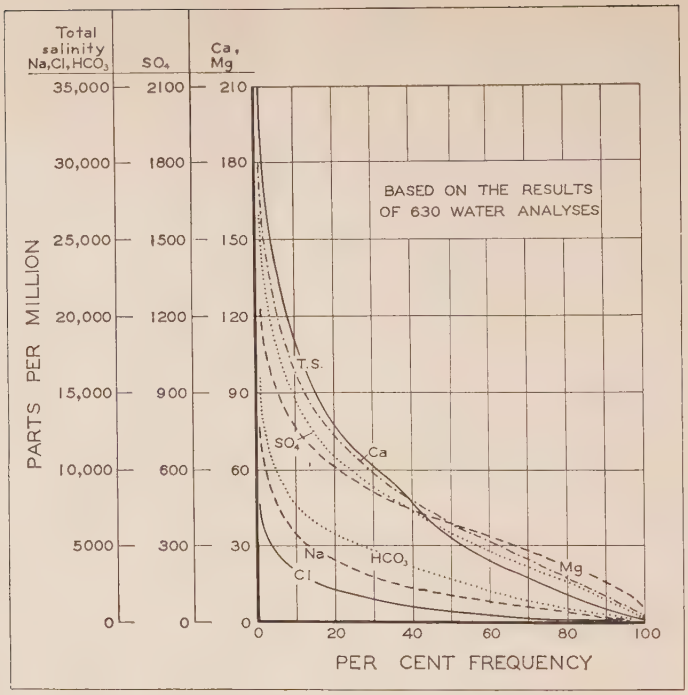


Fig. 15. Integral frequency curves of chemical composition of bicarbonate waters in oilfield areas (T.S. = total salinity).

*Table* 32. *Depth of occurrence in subterranean waters in oilfield areas of the world*

A. *Distribution of chloride waters*

| *Rating of depth (feet)* | *Occurrence* | | *Rating of depth (feet)* | *Occurrence* | |
|---|---|---|---|---|---|
| | *Number* | *Percent* | | *Number* | *Percent* |
| 0–2,000 | 133 | 22·0 | 8,000–10,000 | 42 | 7·0 |
| 2,000–4,000 | 260 | 43·0 | 10,000–12,000 | 14 | 2·3 |
| 4,000–6,000 | 93 | 15·4 | 12,000–14,000 | 2 | 0·3 |
| 6,000–8,000 | 61 | 10·0 | | | |
| | | | Total | 605 | 100·0 |

B. *Frequency*

| *Major groups of waters* | *Frequency in percent* | | | | | | | *Number of wells** |
|---|---|---|---|---|---|---|---|---|
| | 1·0 | 10·0 | 25·0 | 50·0 | 75·0 | 90·0 | 99·0 | |
| Bicarbonate | 6,225 | 4,142 | 3,175 | 2,282 | 1,587 | 1,091 | 520 | 34 |
| Sulphate | 5,100 | 3,393 | 2,600 | 1,869 | 1,300 | 894 | 426 | 28 |
| Chloride | 11,328 | 7,095 | 5,178 | 3,488 | 2,195 | 1,372 | 509 | 605 |

* *Remarks:* Although the number of wells for bicarbonate and sulphate waters is inadequate compared to chloride waters, the figures show that the former occur at more shallow depth than the latter one. Many pools are now being developed at depths below 10,000 feet, and the deepest bore as yet known has been past the 20,000-feet mark in Wyoming oilfield (Levorsen, 1951; Salnikov, 1951).

*Table* 33. *Chemical composition of bicarbonate waters associated with oil-pools in world*

| *Percent frequency* | *Mode of reporting* | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3$ | *Total salinity* |
|---|---|---|---|---|---|---|---|---|
| 1·0 | p.p.m. | 12,578 | 176 | 126 | 7,742 | 1,607 | 15,604 | 37,830 |
| | Reacting value % | 48·3 | 0·8 | 0·9 | 21·6 | 3·1 | 25·3 | 100·0 |
| 10·0 | p.p.m. | 5,977 | 97 | 77 | 3,500 | 890 | 7,859 | 18,400 |
| | Reacting value % | 47·9 | 0·8 | 1·3 | 20·1 | 3·6 | 26·3 | 100·0 |
| 25·0 | p.p.m. | 3,497 | 65 | 56 | 1,946 | 596 | 5,264 | 11,424 |
| | Reacting value % | 47·5 | 1·0 | 1·5 | 17·8 | 4·0 | 28·2 | 100·0 |
| 50·0 | p.p.m. | 1,587 | 38 | 38 | 812 | 346 | 2,820 | 5,636 |
| | Reacting value % | 46·6 | 1·3 | 2·1 | 15·0 | 4·6 | 30·4 | 100·0 |
| 75·0 | p.p.m. | 595 | 20 | 24 | 294 | 181 | 1,316 | 2,430 |
| | Reacting value % | 44·9 | 1·7 | 3·4 | 12·3 | 5·5 | 32·2 | 100·0 |
| 90·0 | p.p.m. | 174 | 9 | 15 | 70 | 86 | 564 | 918 |
| | Reacting value % | 41·2 | 2·2 | 6·6 | 7·3 | 7·0 | 35·7 | 100·0 |
| 99·0 | p.p.m. | 25 | 2 | 6 | 14 | 22 | 113 | 182 |
| | Reacting value % | 31·3 | 3·1 | 15·6 | 8·0 | 9·0 | 33·0 | 100·0 |
| | $C_v$ | 1·1 | 0·8 | 0·6 | 1·2 | 0·8 | 0·9 | 1·2 |
| Number of analyses | | 618 | 630 | 629 | 629 | 629 | 630 | 630 |

The data in Table 34 show that the water in the productive well is evidently in an active exchange with the surface water or with shallow underground water of lower salinity.

*Table* 34. *Modification of bicarbonate waters in Grozny oilfield* (Lindtrop, 1927) (*Depth* 2,615 *feet*)

| *Analyses* | *Total salinity* (*p.p.m.*) | *Reacting value in percent* | | | *Class of water* | *Remarks* |
|---|---|---|---|---|---|---|
| | | Cl | $SO_4$ | $CO_3$ | | |
| Average (5 analyses) for four years | 1,070 | 10·5 | 24·0 | 15·5 | III | — |
| Average (3 analyses) | 873 | 12·4 | | 37·6 | II | Well was shut in for 3½ months |
| Average (3 analyses) | 957 | 12·7 | 7·4 | 29·9 | III | After twenty hours pumping |
| Average (3 analyses) | 963 | 10·9 | 23·7 | 15·4 | III | After two days pumping |

For four years of pumping a relative equilibrium between the "deep-seated" underground water and surface water has been well established.

However, as the well was shut in for $3\frac{1}{2}$ months the water of higher salinity has accumulated at and near the well. As the pumping renews, this water became depleted and a supply of fresh water from the outside source has reached the

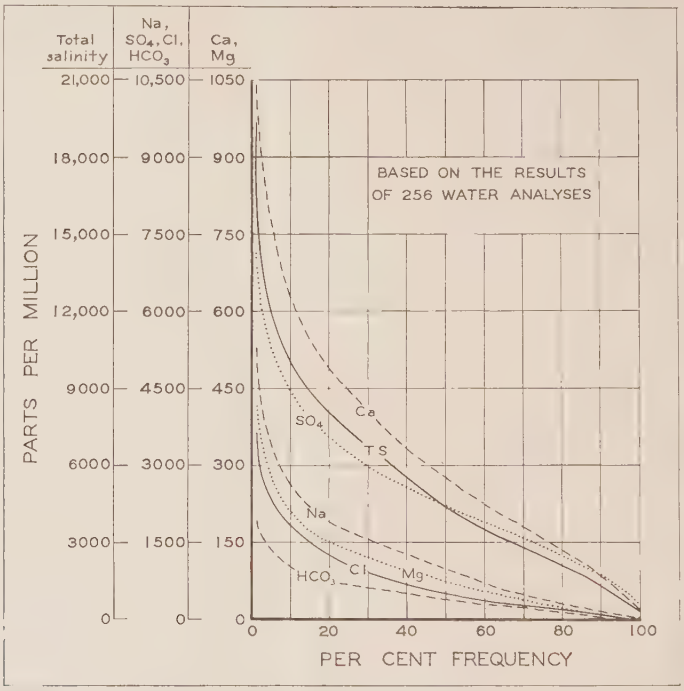


Fig. 16. Frequency curves of chemical composition of sulphate waters in oilfield areas (T.S. = total salinity).

pumped well: total salinity of water sharply decreased and the $CO_3$ content increased accordingly. $SO_4$-ion disappeared completely. After twenty hours pumping and particularly after two days the chemical composition of water became nearly the same as it was for four years. This is clear evidence that the supply from the outside source was inadequate to cover the pumpage, and the "deep-seated" ("native") water came up again.

The water analysis given in Table 35 can be considered as a representative analysis of highly concentrated bicarbonate waters (Class II) associated with oil-pools:

*Table* 35. *Representative analysis of highly-concentrated bicarbonate waters* (Crawford, 1942)

| *Total salinity* (*p.p.m.*) | *Reacting value in percent* | | | | | |
|---|---|---|---|---|---|---|
| | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3 + CO_3$ |
| 76,439 | 50·0 | 0 | 0 | 18·8 | 0·6 | 30·6 |

*Sulphate waters*—The variation in chemical composition of sulphate waters is characterized by the data tabulated in Table 36 and presented in Fig. 16.

*Table* 36. *Chemical composition of sulphate waters associated with oil-pools in world*

| *Percent frequency* | *Mode of reporting* | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3$ | *Total salinity* |
|---|---|---|---|---|---|---|---|---|
| 1·0 | p.p.m. | 5,113 | 1,066 | 415 | 3,624 | 7,169 | 1,934 | 19,321 |
| | Reacting value % | 32·7 | 11·8 | 5·5 | 18·5 | 25·9 | 5·6 | 100·0 |
| 10·0 | p.p.m. | 2,575 | 629 | 209 | 1,812 | 4,488 | 1,071 | 10,992 |
| | Reacting value % | 34·9 | 9·8 | 5·3 | 16·0 | 28·6 | 5·4 | 100·0 |
| 25·0 | p.p.m. | 1,725 | 441 | 140 | 1,111 | 3,273 | 718 | 7,407 |
| | Reacting value % | 34·6 | 10·1 | 5·3 | 14·4 | 30·3 | 5·3 | 100·0 |
| 50·0 | p.p.m. | 924 | 275 | 75 | 551 | 2,207 | 416 | 4,448 |
| | Reacting value % | 33·5 | 11·5 | 5·0 | 11·6 | 33·4 | 5·0 | 100·0 |
| 75·0 | p.p.m. | 431 | 159 | 35 | 228 | 1,388 | 218 | 2,459 |
| | Reacting value % | 31·8 | 12·5 | 5·7 | 8·5 | 37·1 | 4·4 | 100·0 |
| 90·0 | p.p.m. | 185 | 84 | 15 | 79 | 868 | 104 | 1,335 |
| | Reacting value % | 30·0 | 15·7 | 4·3 | 3·0 | 43·0 | 4·0 | 100·0 |
| 99·0 | p.p.m. | 37 | 26 | 3 | 8 | 322 | 26 | 422 |
| | Reacting value % | 26·0 | 20·8 | 3·2 | 1·4 | 45·8 | 2·8 | 100·0 |
| | $C_v$ | 0·9 | 0·7 | 0·9 | 1·0 | 0·6 | 0·8 | 0·9 |
| Number of analyses | | 256 | 256 | 256 | 256 | 256 | 256 | 256 |

*Chloride waters*—The chemical composition of chloride waters is illustrated by the data in Table 37 and Fig. 17.

*Typical characteristics of oilfield waters*—The typical chemical characteristics of subterranean waters of different genetic types associated with oil-pools in the world are illustrated by the data presented in Table 38.

*Hydraulic gradients and velocity of flow of oilfield waters*

A diluted water in oilfields similar to the other subsurface reservoirs indicates a freedom of circulation of water, whereas a more concentrated water manifests sluggish flow or stagnant conditions.

Waters associated with oil-pools are usually under a variable pressure which is thought to be caused by the effective hydrostatic head, overburden, and the rate of fluid movement through reservoir media. This pressure is something as great as 300 atmospheres at a depth of 10,000 feet (Funkhauser *et. al.* 1948).

In Cushing oilfield, for instance, the hydraulic gradients rate between 0·02 and

0·04 at a depth of 1,700 to 1,850 feet below sea-level (Beal, 1917); the gradient 0·02 is also known in Terek-Dagestan oil-pools.

The rate of movement of waters evidently varies in an irregular manner, being in many cases affected by the numerous faults and fractures. In Salt Creek oil-field, for example, water moves at the rate of 1 to 4 feet per 24 hours (Coffin and Deford, 1934).

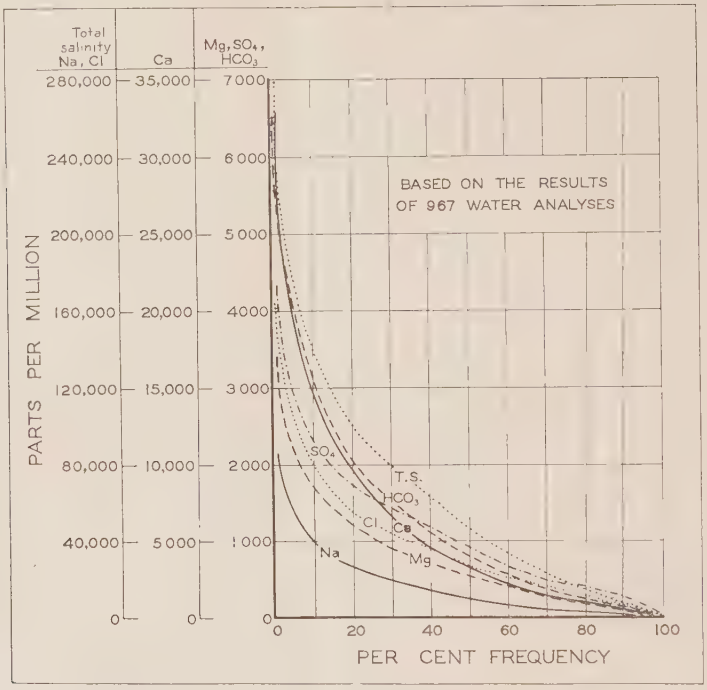


Fig. 17. Frequency curves of chemical composition of chloride waters in oilfield areas (T.S. = total salinity).

It is assumed that water and oil in the subsurface reservoir are in static equilibrium before the reservoir is tapped by drilling wells, but as oil is produced the encroachment of water into the space previously occupied by oil occurs.

Among the forces which may be responsible for the water entering (expansibility of the water due to the presence of dissolved gases, reduction in pore space of the rock upon reduction of pressure, etc.) the supply of extraneous water either at the outcrop of the formation or from other formations along fissures and cracks in the faulted and sheared zones might be an important factor (Wilde and Moore, 1938).

The present circulation of subterranean waters has certainly modified the distribution of oil and gas in some oilfields (the Grey Bull and Torchlight fields, for instance) (Lloyd and Brindenstine, 1922).

On the other hand, in the formations which to all appearance contain no water and where liquids are considered to be in a "static" condition there is no hydraulic force, and, in contrast to the structural occurrence of oil, the oil-pools in such formations are found in the synclines (Reeves, 1917).

*Table* 37. *Chemical composition of chloride waters associated with oil-pools in world*

| *Percent frequency* | *Mode of reporting* | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3$ | *Total salinity* |
|---|---|---|---|---|---|---|---|---|
| 1·0 | p.p.m. | 86,190 | 32,627 | 3,496 | 161,020 | 4,315 | 6,327 | 293,975 |
| | Reacting value % | 33·0 | 14·5 | 2·5 | 48·0 | 0·9 | 1·1 | 100·0 |
| 10·0 | p.p.m. | 40,970 | 14,750 | 1,748 | 81,092 | 2,330 | 3,007 | 143,897 |
| | Reacting value % | 33·4 | 13·8 | 2·8 | 48·0 | 1·0 | 1·0 | 100·0 |
| 25·0 | p.p.m. | 23,970 | 8,201 | 1,071 | 54,320 | 1,601 | 1,760 | 90,923 |
| | Reacting value % | 33·8 | 13·3 | 2·9 | 48·0 | 1·0 | 1·0 | 100·0 |
| 50·0 | p.p.m. | 10,880 | 3,422 | 532 | 29,100 | 928 | 798 | 45,660 |
| | Reacting value % | 34·3 | 12·4 | 3·3 | 48·1 | 1·1 | 0·8 | 100·0 |
| 75·0 | p.p.m. | 4,080 | 1,239 | 220 | 13,580 | 487 | 300 | 19,906 |
| | Reacting value % | 34·5 | 12·0 | 3·5 | 48·1 | 1·2 | 0·7 | 100·0 |
| 90·0 | p.p.m. | 1,190 | 295 | 76 | 5,820 | 232 | 87 | 7,700 |
| | Reacting value % | 35·7 | 10·3 | 4·0 | 48·2 | 1·4 | 0·4 | 100·0 |
| 99·0 | p.p.m. | 170 | 59 | 8 | 1,164 | 58 | 12 | 1,471 |
| | Reacting value % | 33·0 | 14·0 | 3·0 | 48·0 | 1·7 | 0·3 | 100·0 |
| | $C_v$ | 1·1 | 1·2 | 1·0 | 0·9 | 0·8 | 1·1 | 1·0 |
| | Number of analyses | 939 | 933 | 939 | 943 | 940 | 936 | 967 |

*Table* 38. *Chemical characteristics of typical waters associated with oil-pools in the world* (50 *per cent frequency*)

| *Major groups of waters* | *Mode of reporting* | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3$ | *Total salinity* |
|---|---|---|---|---|---|---|---|---|
| Bicarbonate | p.p.m. | 1,587 | 38 | 38 | 812 | 346 | 2,820 | 5,636 |
| | Reacting value % | 46·6 | 1·3 | 2·1 | 15·0 | 4·6 | 30·4 | 100·0 |
| Sulphate | p.p.m. | 924 | 275 | 75 | 551 | 2,207 | 416 | 4,448 |
| | Reacting value % | 33·5 | 11·5 | 5·0 | 11·6 | 33·4 | 5·0 | 100·0 |
| Chloride | p.p.m. | 10,880 | 3,422 | 532 | 29,000 | 928 | 798 | 45,660 |
| | Reacting value % | 34·3 | 12·4 | 3·3 | 48·1 | 1·1 | 0·8 | 100·0 |

*Remarks:* These characteristics are different from those shown elsewhere (Chebotarev, 1952), because the number of analyses was different.

*Practical view*—The practice in search for oil shows that a successful correlation and identification of subterranean waters by chemical analyses has often saved time and reduced the cost of operations.

The frequency curves compiled for the different types of water associated with oil-pools are considered as a basis for such correlation.

The frequency of 50 per cent has been taken as a typical characteristic for salinity variation of subterranean waters (Chebotarev, 1951, 1952).

For a given statistical aggregate (Table 33, for instance) the frequency of 50 per cent corresponds to the value of 5,636 p.p.m. of total salinity, which will be taken as a typical salinity for bicarbonate waters in oil-pools of the world.

Using this frequency for any chemical characteristic, we can find qualitative value for subterranean water (Na, Ca, Mg, Cl, $SO_4$, $HCO_3$).

Thus, according to the integral curve for total salinity of bicarbonate waters (Fig. 15), we can foresee that four out of every ten bores find water of 7,000 p.p.m.; every second bore (e.g., 50 per cent frequency) 5,636 p.p.m.; seven out of every ten 4,000 p.p.m., and so on.

For example, it is required to determine the chance of finding oil in the Great Artesian Basin, where waters of bicarbonate type prevail. By plotting the frequency curve of salinity of the Jurassic waters (Table 28) it is easy to ascertain that there is a 2 per cent probability of finding waters which are typical of oil-pools.

The petroliferous possibilities of the region would appear to depend also upon there being favourable geothermal conditions, but unfortunately no bore has been drilled in the favourable area deep enough to pierce a zone of geothermal optimum.

## *Chemical composition of natural brines*

*Oilfield brines.*

The representative analyses of natural brines associated chiefly with oil-pools are given in Table 39.

*Table* 39. *Chemical composition of natural brines*

| *Depth (feet)* | *Mode of reporting* | *Total salinity* | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3$ | *Remarks* | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | *Occurrence* | *Reference* |
| 3,050 | p.p.m. | 55,000 | 16,940 | 2,540 | 1,015 | 34,130 | 275 | 96 | Oil-pool, | 57 |
| | React. value % | — | 38·9 | 6·7 | 4·4 | 49·5 | 0·4 | 0·1 | Kansas | |
| — | p.p.m. | 76,100 | 1,300 | 19,500 | 4,900 | 50,400 | — | — | Calcium | 50 |
| | React. value % | — | 2·0 | 34·0 | 14·1 | 50·0 | — | — | work, Ohio | |
| 1,225 | p.p.m. | 150,400 | 47,600 | 6,550 | 2,208 | 93,905 | — | 102 | Oil-pool, | 57 |
| | React. value % | — | 40·1 | 3·6 | 6·3 | 49·9 | — | 0·1 | Kansas | |
| 3,450 | p.p.m. | 250,000 | 75,600 | 14,000 | 3,351 | 156,744 | — | 48 | Oil-pool, | 57 |
| | React. value % | — | 38·6 | 8·2 | 3·2 | 50·0 | — | — | Kansas | |
| — | p.p.m. | 300,000 | — | — | — | — | — | — | Oil-pool, | 27 |
| | React. value % | — | 27·0 | 21·0 | 2·0 | 50·0 | trace | trace | Alberta | |
| 2,700 | p.p.m. | 425,900 | 144,500 | 16,600 | 4,200 | 258,800 | 1,800 | — | Oil-pool, | 50 |
| | React. value % | — | 42·2 | 5·5 | 2·3 | 49·9 | 0·1 | — | Ohio | |

*Remarks:* Own computation.

*Table* 40. *Variation in salinity concentration in "connate" brines of Eastern Kentucky* (McGrain and Thomas, 1951)

A. *Distribution*

Total salinity

| *Rating* (*p.p.m.*) | *Occurrence* | | *Rating* (*p.p.m.*) | *Occurrence* | |
|---|---|---|---|---|---|
| | *Number* | *Percent* | | *Number* | *Percent* |
| 0–40,000 | 12 | 26·6 | 120,000–160,000 | 12 | 26·6 |
| 40,000–80,000 | 9 | 20·0 | 160,000–200,000 | 4 | 9·0 |
| 80,000–120,000 | 7 | 15·6 | More than 200,000 | 1 | 2·2 |
| — | — | — | Total | 45 | 100·0 |

$\frac{Ca^{++}}{Mg^{++}}$ ratio

| *Rating of ratios* | *Occurrence* | | *Rating of ratios* | *Occurrence* | |
|---|---|---|---|---|---|
| | *Number* | *Percent* | | *Number* | *Percent* |
| 0–2 | 4 | 9·1 | 8–10 | — | — |
| 2–4 | 30 | 68·2 | 10–12 | — | — |
| 4–6 | 7 | 15·9 | 12–14 | 1 | 2·3 |
| 6–8 | 2 | 4·5 | Total | 44 | 100·0 |

B. *Integral frequency*

| *Number of analyses* | *Characteristics* | *Frequency in percent* | | | | | $C_v$ |
|---|---|---|---|---|---|---|---|
| | | 1·0 | 25·0 | 50·0 | 75·0 | 90·0 | |
| 45 | Total salinity p.p.m. | 265,880 | 121,440 | 81,880 | 51,520 | 32,000 | 0·6 |
| 44 | $\frac{Ca^{++}}{Mg^{++}}$ | 8·9 | 4·6 | 3·3 | 2·3 | 1·6 | 0·5 |

It has been stated that in Ohio, for instance, the quantity of brine that has been taken from Big salt sand was enormous and much more than the rock could at any time contain; on the other hand, in Pittsburgh the natural brines became so dilute that it was no longer profitable to work them (Bownocker, 1906; Phalen, 1919).

*"Connate" brines*

The variation in total salinity of Appalachian brines which serve for industrial uses and are considered as "connate" waters is illustrated by the data in Table 40.

*Change in salinity concentration of brines*

The increase in salinity concentration of brines as oil production continued is shown in Table 41.

*Table* 41. *Change in salinity concentration of brines as production of oil continued* (*Ohio*)
(Mills *and* Wells, 1919)

| *Depth of water* (*feet*) | *Analyzed when the well was* | *Total salinity* (*p.p.m.*) | $Ca^{..}$ $Mg^{..}$ |
|---|---|---|---|
| 1,465 | 1 month old | 79,150 | 5·4 |
| | 18 months old | 103,730 | 5·6 |

The Excelsior Company Works, however, have pumped chloride brines from the 750-feet level for many years without any substantial change in the chemical composition (Mills and Wells, 1919).

*Salt domes and associated waters*

In the general consensus the salt domes have been derived from sedimentary salt deeply buried in the strata under the action of the great gravity or tectonic upward forces.

It is believed that rock-salt which is of lower specific gravity than the sediments has been displaced as a plastic body and has often pierced the adjacent sedimentary rocks.

As regards the position of subterranean waters with respect to the salt body, the following three types of water have been determined (Dzens-Litovsky, 1945): 1. Oversalt waters, chiefly brines, circulate over the salt in the cover-rocks; they are agents in the formation of the intensive karst cavities occurring often in salt mines. 2. Lateral or near-salt waters (brines) surround the salt deposits from the sides; they occur at the contact of the salt with the rocks surrounding the salt body. 3. Inter-salt and under-salt waters (brines) which are found in rocks inter and under the salt deposit respectively.

*Subterranean waters of volcanic association*

*Waters of geysers.*

The chemical composition of thermal waters of volcanic association is shown in Table 42.

*Table* 42. *Chemical composition of thermal waters of volcanic association* (*U.S.A.*)
(Stearns *et al.*, 1937)

| *Locality* | *Mode of reporting* | *Total salinity* | Na | K | Ca | Mg | Cl | $SO_4$ | $HCO_3$ | *Temperature* °C |
|---|---|---|---|---|---|---|---|---|---|---|
| Geyser Beowawe Nevada | p.p.m. | 1,208 | 239 | 33 | 2·0 | — | 47 | 97 | 129 | Boiling |
| | React. value % | — | 45·1 | 4·3 | 0·6 | — | 12·0 | 18·2 | 19·8 | |
| Steamboat Spring No. 21, Nevada | p.p.m. | 2,596 | 695 | 74 | 8·7 | 1·0 | 921 | 156 | 276 | 83·9 |
| | React. value % | — | 46·3 | 2·9 | 0·7 | 0·1 | 38·5 | 4·7 | 6·8 | |
| Sulphur Bank, California | p.p.m. | 8,245 | 1,389 | 68·1 | 56·3 | 57·1 | 489 | 1,984 | 1,891 | 80·6 |
| | React. value % | — | 35·3 | 10·3 | 1·6 | 2·8 | 8·0 | 24·0 | 18·0 | |

*Remarks:* Reacting values in percent have been computed with approximation.

*Waters of mud volcanoes.*

The data presented in Table 43 illustrate the salinity concentration and the ionic content in the waters that have occurred with oil and gas in mud volcanoes.

*Table* 43. *Chemical composition of waters associated with mud volcanoes (Turkmenia)* (KOSSYGIN, 1935)

| *Locality* | *Total salinity (p.p.m.)* | *Reacting value in percent** | | | | | | *Temperature of water* °F |
|---|---|---|---|---|---|---|---|---|
| | | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3 + CO_3$ | |
| Cheleken No. 1 | 251,800 | 35·8 | 11·2 | 3·0 | 50·00 | — | — | — |
| No. 2 | 43,360 | 49·7 | 0·1 | 0·2 | 44·8 | 0·9 | 4·3 | — |
| No. 3 | 238,000 | 36·8 | 10·8 | 2·4 | 49·98 | 0·02 | — | — |
| Neftedag No. 4 | 144,800 | 40·7 | 7·3 | 2·0 | 49·8 | 0·2 | — | 126 |
| Boyadag No. 5 | 265,000 | 39·8 | 8·2 | 2·0 | 50·0 | — | — | 126 |
| Keimir No. 6 | 27,300 | 48·0 | 1·2 | 0·8 | 47·2 | — | 2·8 | 90 |
| No. 7 | 414,000 | 42·8 | — | 7·2 | 41·7 | 7·3 | 1·0 | 90 |

* With approximation.

*Salinity of water associated with metalliferous deposits*

The data in Table 44 show the range of salinity variation of subterranean water found in zinc and lead deposits.

*Table* 44. *Salinity variation of water associated with zinc and lead deposits of the Jopkin Region, U.S.A.* (SIEBENTAL, 1915)

A. *Distribution*

| *Rating of total salinity (p.p.m.)* | *Occurrence* | | *Rating of total salinity (p.p.m.)* | *Occurrence* | |
|---|---|---|---|---|---|
| | *Number* | *Percent* | | *Number* | *Percent* |
| 0–5,000 | 93 | 78·1 | 20,000–25,000 | 2 | 1·7 |
| 5,000–10,000 | 8 | 6·7 | 25,000–30,000 | 1 | 0·9 |
| 10,000–15,000 | 8 | 6·7 | 30,000–35,000 | 0 | 0 |
| 15,000–20,000 | 3 | 2·5 | More than 35,000 | 4 | 3·4 |
| | | | TOTAL | 119 | 100·0 |

B. *Frequency*

| *Salinity* | *Percent frequency* | | | | | | *Number of analyses* | $C_v$ |
|---|---|---|---|---|---|---|---|---|
| | 1·0 | 10·0 | 25·0 | 50·0 | 75·0 | 90·0 | | |
| Total salinity (p.p.m.) | 36,180 | 15,600 | 8,400 | 3,180 | 1,020 | 240 | 119 | 1·3 |

*Remarks:* The data in Tables A and B have been computed by the present author.

It has been suggested that for the leaching of zinc from the Cambrian and Ordovician dolomite limestone in the Joplin Region the pore-water would require to be changed thirteen times.

*Salinity of waters from sedimentary, metamorphic, and igneous rocks.*

*Sedimentary rocks.*

The salinity variation in subterranean waters from sedimentary formations is illustrated by the data in Table 45.

*Table 45. Salinity of shallow underground water from Recent-Pleistocene Continental deposits (Europe) (Author's data)*

| *Percent frequency* | *Total salinity* | *Parts per million* | | | | | *Hardness in English degrees* |
|---|---|---|---|---|---|---|---|
| | | Na + K | Ca | Mg | Cl | $SO_4$ | |
| 1·0 | 8,880 | 2,378 | 580 | 762 | 1,380 | 1,850 | 207·0 |
| 10·0 | 4,440 | 936 | 342 | 312·3 | 655 | 876 | 104·2 |
| 25·0 | 2,710 | 462 | 240 | 158·6 | 383 | 513 | 69·7 |
| 50·0 | 1,350 | 135 | 150 | 54·7 | 174 | 233 | 37·4 |
| 75·0 | 568 | 33·8 | 86·4 | 15·2 | 65·3 | 87·5 | 17·4 |
| 99·0 | 19·3 | 0 | 14·1 | 1·2 | 2·7 | 3·6 | 1·5 |
| Number of analyses | 616 | 72 | 203 | 179 | 876 | 412 | 806 |

*Table 46. Salinity of subterranean waters from Recent-Pleistocene formation (Australia)* (Miles, 1952)

| *Salinity* | *Percent frequency* | | | | | | | *Number of analyses* | $C_v$ |
|---|---|---|---|---|---|---|---|---|---|
| | 1·0 | 10·0 | 25·0 | 50·0 | 75·0 | 90·0 | 99·0 | | |
| Total salinity (p.p.m.) | 29,357 | 11,554 | 5,720 | 1,637 | 415 | 85 | — | 323 | 1·9 |

*Remarks:* Own computation.

*Table 47. Salinity of subterranean waters from Tertiary formations (Europe) (Author's data)*

| *Percent frequency* | *Total salinity* | *Parts per million* | | | | | | *Hardness in English degrees* |
|---|---|---|---|---|---|---|---|---|
| | | Na + K | Ca | Mg | Cl | $SO_4$ | $HCO_3$ | |
| 1·0 | 10,442 | 5,704 | 589 | 363 | 5,120 | 966 | 647 | 134 |
| 10·0 | 6,947 | 2,852 | 294 | 183 | 3,406 | 487 | 405 | 89 |
| 25·0 | 5,324 | 1,748 | 180 | 123 | 2,611 | 326 | 296 | 68 |
| 50·0 | 3,827 | 868 | 90 | 66 | 1,877 | 175 | 199 | 49 |
| 75·0 | 2,662 | 360 | 37 | 31 | 1,224 | 81 | 125 | 34 |
| 90·0 | 1,830 | 124 | 13 | 13 | 898 | 35 | 78 | 24 |
| 99·0 | 837 | 12 | 1·3 | 3 | 428 | 7 | 29 | 11 |
| $C_v$ | 0·5 | 1·0 | 1·0 | 0·9 | 0·5 | 0·9 | 0·6 | 0·5 |
| Number of analyses | 993 | 174 | 546 | 464 | 1,631 | 765 | 206 | 1,649 |

*Table* 48. *Salinity of subterranean waters from Tertiary formations of Counties Albert and Alfred (Australia)* (BARNES, 1951)

| *Salinity* | *Percent frequency* | | | | | | | *Number of analyses* | $C_v$ |
|---|---|---|---|---|---|---|---|---|---|
| | 1·0 | 10·0 | 25·0 | 50·0 | 75·0 | 90·0 | 99·0 | | |
| Total salinity (p.p.m.) | 10,040 | 6,680 | 5,120 | 3,680 | 2,400 | 1,760 | 840 | 592 | 0·5 |

*Remarks:* All computations have been done by the present writer.

*Table* 49. *Salinity of subterranean waters from Tertiary (Miocene-Oligocene) (Australia)* (MILES, 1952)

| *Salinity* | *Percent frequency* | | | | | | | *Number of analyses* | $C_v$ |
|---|---|---|---|---|---|---|---|---|---|
| | 1·0 | 10·0 | 25·0 | 50·0 | 75·0 | 90·0 | 99·0 | | |
| Total salinity (p.p.m.) | 5,377 | 3,360 | 2,460 | 1,659 | 1,044 | 658 | 243 | 240 | 0·6 |

*Remarks:* Own computation.

*Table* 50. *Salinity of subterranean waters from Mesozoic formations (Europe) (Author's data)*

| *Percent frequency* | *Total salinity* | *Parts per million* | | | | | *Hardness in English degrees* |
|---|---|---|---|---|---|---|---|
| | | Ca | Mg | Cl | $SO_4$ | $HCO_3$ | |
| 1·0 | 36,610 | 3,340 | 2,626 | 11,248 | 1,079 | 685 | 314 |
| 10·0 | 14,440 | 1,315 | 1,190 | 4,432 | 543 | 487 | 124 |
| 25·0 | 7,150 | 650 | 660 | 2,192 | 364 | 394 | 61 |
| 50·0 | 2,084 | 190 | 276 | 640 | 195 | 301 | 17 |
| 75·0 | 521 | 48 | 100 | 160 | 91 | 225 | 7·5 |
| 99·0 | 0 | 0 | 5 | 32 | 8 | 98 | 0·8 |
| $C_v$ | — | — | — | 2·0 | 0·9 | — | 1·7 |
| Number of analyses | 105 | 96 | 96 | 211 | 130 | 43 | 222 |

*Table 51. Salinity of subterranean waters from Paleozoic formations (Europe)*
*(Author's data)*

| *Percent frequency* | *Parts per million* | | | *Hardness in English degrees* | *Class of water* |
|---|---|---|---|---|---|
| | Cl | $SO_4$ | $HCO_3$ | | |
| 1·0 | 613 | 2,407 | 753 | 157 | IV |
| 10·0 | 384 | 1,212 | 501 | 78 | IV |
| 25·0 | 240 | 812 | 384 | 48 | IV |
| 50·0 | 189 | 435 | 276 | 24 | IV |
| 75·0 | 119 | 203 | 192 | 10 | IV |
| 90·0 | 74 | 87 | 132 | 3 | III |
| 99·0 | 28 | 17 | 63 | 0·4 | III |
| $C_v$ | 0·6 | 0·9 | 0·5 | 1·0 | — |
| Number of analyses | 910 | 707 | 418 | 994 | — |

*Table 52. Salinity of subterranean waters from Paleozoic formations (Union of South Africa)*
(Bond, 1946)

| *Salinity* | *Percent frequency* | | | | | | | $C_v$ | *Number of analyses* |
|---|---|---|---|---|---|---|---|---|---|
| | 1·0 | 10·0 | 25·0 | 50·0 | 75·0 | 90·0 | 99·0 | | |
| Total salinity (p.p.m.) | 3,253 | 1,638 | 1,098 | 588 | 274 | 118 | 24 | 0·9 | 161 |
| $\frac{Ca^{\cdot\cdot}}{Mg^{\cdot\cdot}}$ | 5·5 | 2·7 | 1·7 | 0·8 | 0·2 | 0·12 | 0·01 | 1·0 | 167 |

The representative analyses of water of the high salinity concentration associated with the Paleozoic formations are given in Table 53.

*Table 53. Chemical composition of Paleozoic waters of the high salinity (south-eastern Kansas)*
(Abernathy, 1948)

| *Formation* | *Location of wells* | *Parts per million* | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | *Total salinity* | Na | Ca | Mg | Cl | $SO_4$ | $HCO_3$ |
| Pennsylvanian | Sect. 28T.25S RSE | 191,499 | 60,786 | 8,890 | 3,200 | 118,560 | — | 63·0 |
| Mississippian | Sect. 8.T.28S R.II E. | 106,199 | 33,860 | 4,731 | 1,791 | 65,786 | 4·0 | 27·0 |

*Metamorphic rocks.*

Total salinity of shallow underground waters from metamorphic rocks can be characterized by the data in Tables 54 and 55.

*Table* 54. *Salinity of subterranean waters from metamorphic rocks* (*Union of South Africa*) (Bond, 1946)

| *Ingredients* | *Percent frequency* | | | | | | | $C_v$ | *Number of analyses* |
|---|---|---|---|---|---|---|---|---|---|
| | 1·0 | 10·0 | 25·0 | 50·0 | 75·0 | 90·0 | 99·0 | | |
| Total salinity (p.p.m.) | 11,248 | 4,432 | 2,192 | 640 | 160 | 32 | — | 1·7 | 88 |
| $\frac{Ca^{\cdot\cdot}}{Mg^{\cdot\cdot}}$ | 5·5 | 2·7 | 1·7 | 0·8 | 0·2 | 0·12 | 0·01 | 1·0 | 96 |

*Table* 55. *Salinity of subterranean waters from metamorphic* (*Pre-Cambrian*) *rock* (*Australia*) (Miles, 1952)

| *Salinity* | *Percent frequency* | | | | | | | *Number of analyses* | $C_v$ |
|---|---|---|---|---|---|---|---|---|---|
| | 1·0 | 10·0 | 25·0 | 50·0 | 75·0 | 90·0 | 99·0 | | |
| Total salinity (p.p.m.) | 4,018 | 2,674 | 2,045 | 1,473 | 958 | 700 | 343 | 31 | 0·5 |

*Remarks:* Own computation.

*Igneous rocks.*

The salinity variation in subterranean waters found in igneous rocks is illustrated by the data in Tables 56, 57.

*Table* 56. *Salinity of subterranean water from igneous rocks* (*Europe*) (*Author's data*)

| *Percent of frequency* | *Parts per million* | | | | | *Hardness in English degrees* |
|---|---|---|---|---|---|---|
| | *Total salinity* | Ca | Mg | Cl | $SO_4$ | |
| 1·0 | 3,600 | 448 | 145 | 468 | 544 | 93·9 |
| 10·0 | 1,810 | 298 | 73 | 185 | 214 | 58·7 |
| 25·0 | 1,212 | 228 | 49 | 91 | 106 | 42·9 |
| 50·0 | 650 | 164 | 26 | 27 | 31 | 28·8 |
| 75·0 | 304 | 114 | 12 | 7 | 8 | 18·2 |
| 99·0 | 26 | 38 | 1·0 | 0 | 0 | 4·2 |
| Number of analyses | 314 | 270 | 260 | 377 | 308 | 370 |

The data presented in Tables 52, 54, 57 have been computed by the present writer. The permission for the reference on this publication is given by the Government Printer, Pretoria. It has been suggested that the following imprint must be given; "Extract from Geological Memoir No. 41 reproduced under Government Printers Copyright Authority No. 1120 of 30/1/53."

*Table 57. Salinity of subterranean waters from igneous rocks (Union of South Africa)* (Bond, 1946)

| *Ingredients* | *Percent frequency* | | | | | | | $C_v$ | *Number of analyses* |
|---|---|---|---|---|---|---|---|---|---|
| | 1·0 | 10·0 | 25·0 | 50·0 | 75·0 | 90·0 | 99·0 | | |
| Total salinity (p.p.m.) | 11,400 | 4,487 | 2,219 | 648 | 162 | 32 | — | 1·8 | 175 |
| $\frac{Ca^{\cdot\cdot}}{Mg^{\cdot\cdot}}$ | 15·6 | 6·1 | 3·0 | 0·9 | 0·2 | 0·04 | — | 2·0 | 158 |

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# $A^{40}/K^{40}$ ratios of feldspars and micas from the same rock

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ABSTRACT

$A^{40}/K^{40}$ ratios have been determined for feldspars and micas from the same rock from seven geologic settings. The $A^{40}/K^{40}$ ratio for micas is higher than that for the feldspar in every case.

Because of the widespread occurrence of potassium minerals, the possibility of dating rocks by the $K^{40}$-$A^{40}$ disintegration has received considerable attention in the past several years. If this is to be used as an absolute dating method, it is necessary to assume that the radiogenic argon has been quantitatively retained in the mineral since its formation. In order to test the validity of this assumption we have measured the ratio of radiogenic argon to potassium from feldspars and micas separated from the same rock. If the two minerals are cogenetic and have retained argon quantitatively, the ratios should be the same for the two minerals. The results of these measurements are shown in Table 1.

*Table* 1. *Comparison of* $A^{40}/K^{40}$ *ratios of feldspars and micas from the same rock*

| *Location* | *Rock type* | $A^{40}/K^{40}$ | |
|---|---|---|---|
| | | *feldspar* | *mica* |
| Quartz Creek, Colo. | Granite | 0·0725 | 0·107 |
| Uncompahgre, Colo. | Granite | 0·0709 | 0·109 |
| Capetown, S. Africa | Granite | 0·0105 | 0·0337 |
| Ohio City, Colo. | Pegmatite | 0·0590 | 0·0974 |
| Black Hills, S. Dak. | Pegmatite | 0·0862 | 0·118 |
| Jakkalswater, S. Africa | Pegmatite | 0·0359 | 0·0695 |
| Wilberforce, Ontario | Pegmatite | 0·0614 | 0·0695 |

The radiogenic argon content of the minerals was measured by the conventional techniques of isotope dilution for gaseous samples as developed by Inghram and Hayden, and described by Wasserburg (1954). The potassium analyses were made by isotope dilution as well as with a flame photometer.

The feldspars are seen to have a lower $A^{40}/K^{40}$ ratio than the micas in every case. With the exception of the feldspar from the Cape Granite, which was partially kaolinized, all the samples were fresh. In the case of the Ohio City, Colorado sample the flakes of mica were intergrown with the feldspar used in the determination.

At present we are trying to find the cause of this discrepancy. A comparison of these results with Rb-Sr determinations on the same mineral samples and with U-Pb and Th-Pb determinations on minerals from the same rock, indicates

that the argon age calculated for the mica probably represents a better measure of the true age of the rock than that calculated for the feldspar. These comparisons will be reported in a lengthier paper.

In view of these measurements, calculations of the branching ratio of $K^{40}$ made by comparing $A^{40}/K^{40}$ ratios of feldspars with ages of uraninites, as has been done by Wasserburg and Hayden (1955), must be reconsidered. In the event that the effect reported in this note is caused by the inability of the feldspar to retain argon as completely as the mica, their value of 0·085 for the branching ratio is probably too low.

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